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TRACE AND POTENTIALLY TOXIC ELEMENTS ASSOCIATED WITH URANIUM DEPOSITS IN SOUTH TEXAS

by

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The environmentally sensitive trace elements molybdenum, arsenic, and selenium are concentrated with uranium in ore deposits in South Texas. Cattle grazing in some pastures in mining areas have contracted molybdenosis, a cattle disease resulting from an imbalance of molybdenum and copper. To determine natural concentrations of the elements in soils in the South Texas area and to evaluate possible effects of mining on adjacent agricultural land, two sets of soil samples were collected and analyzed for molybdenum, arsenic, selenium, and copper. Results of the random sampling show that the different geologic formations have different characteristic trace element concentrations.

Sampling in areas of mining and mineralization indicates that high concentrations of molybdenum, arsenic, or selenium occur dominantly in two situations: (1) in areas of shallow mineralization, resulting from natural processes and (2) in drainages adjacent to older abandoned mines, resulting from runoff from the mines. Moderately high concentrations also occur in a few reclaimed areas.

Comparison of molybdenum and copper concentrations in soils and grasses and theoretical considerations of the availability to plants of molybdenum and copper in soils suggest that forage in much of the area studied could have anomalously low copper/molybdenum ratios--low enough to induce molybdenosis in cattle.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meed these needs both efficiently and economically.

This report covers the environmental effects of copper, molybdenum, selenium, and arsenic pollution in relation to uranium deposits in South Texas. Those individuals concerned with existing and potential uranium mining operations should find this report of value. Further information on this subject may be obtained from the Energy Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
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ABSTRACT

The environmentally sensitive trace elements molybdenum, arsenic, and selenium are concentrated with uranium in ore deposits in South Texas. Cattle grazing in some pastures in mining areas have contracted molybdenosis, a cattle disease resulting from an imbalance of molybdenum and copper. To determine natural concentrations of the elements in soils in the South Texas area and to evaluate possible effects of mining on adjacent agricultural land, two sets of soil samples were collected and analyzed for molybdenum, arsenic, selenium, and copper. Two hundred and fifty-six samples were collected in a statistically random design from soils developed on the Whitsett Formation, Catahoula Formation, or Oakville Sandstone, the major uranium hosts of the area, and 182 samples were collected nonrandomly from areas of mining or mineralization to test specific hypotheses concerning the presence and origin of anomalously high concentrations of the elements.

Results of the random sampling show that the different geologic formations have different characteristic trace element concentrations. The Whitsett Formation has higher molybdenum (resulting from minor near-surface mineralization) and lower copper concentrations than the other two formations. With the exception of molybdenum in the Whitsett Formation and copper in all three formations, the trace element concentrations are similar to published average concentrations in soils worldwide.

Sampling in areas of mining and mineralization indicates that high concentrations of molybdenum, arsenic, or selenium occur dominantly in two situations: (1) in areas of shallow mineralization, resulting from natural processes and (2) in drainages adjacent to older abandoned mines, resulting from runoff from the mines. Moderately high concentrations also occur in a few reclaimed areas. Windblown dust from mining areas has not measurably affected trace element concentrations in adjacent areas.

Comparison of molybdenum and copper concentrations in soils and grasses and theoretical considerations of the availability to plants of molybdenum and copper in soils suggest that forage in much of the area studied could have anomalously low copper/molybdenum ratios--low enough to induce molybdenosis in cattle.

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Landowners in the Karnes County area generously allowed access to their land to sample. Also, Continental Oil Company and Exxon Company, U.S.A. allowed sampling on property they owned or leased. Dawn Kaback, Claude Olenick, and Ed Gabrysch of Continental Oil Company and Gerald Ortloff and Mike Barker of Exxon were particularly helpful. The Soil Conservation Service of the U.S. Department of Agriculture, particularly Roy Freeman and Willard Deering of the Karnes County Office, assisted with soil classification and identification.

SECTION 1

INTRODUCTION

Uranium deposits were discovered in Karnes County in South Texas in 1954. The first mining was by the open-pit method and occurred in the late 1950's. Mining and uranium production have increased steadily with a few interruptions owing to fluctuations in the economics of uranium marketing. Texas is currently ranked the nation's third leading producer of uranium (behind Wyoming and New Mexico), solely on the basis of mining in South Texas. Increased demand for energy in the United States has increased exploration and development in the South Texas uranium district.

Several environmentally sensitive trace elements (molybdenum, arsenic, and selenium) are known to be associated with the South Texas uranium deposits (Harshman, 1974). Mining has brought and will continue to bring to the surface material previously buried, thus introducing the potential for contamination of neighboring agricultural areas and water supplies through stockpiling of ore and overburden, from windblown dust from the ore and overburden, and by transport by surface or ground water. In addition, some uranium mineralization occurs near the surface. Uranium was discovered through studies of surface radioactivity, and the earliest production was from deposits less than 15 m deep (Eargle and others, 1975). Thus, high concentrations of the trace elements could occur naturally in soils in mineralized areas.

In 1972, cattle grazing on a ranch in the uranium district that had several abandoned uranium mines and had been used for stockpiling ore contracted molybdenosis (Dollahite and others, 1972). Molybdenosis is a potentially fatal disease of ruminant animals that have eaten forage with excessive molybdenum concentrations. Soils and grass from the ranch had anomalously high molybdenum and low copper concentrations. Possibly before, and certainly since then, there has been considerable concern over the effects of uranium mining on the environment.

Despite the concern over trace metal contamination, little was known (before this study) about background levels of molybdenum or other potentially toxic elements in soils. It was not known if concentrations sufficiently high to be of concern exist in soils in the area and if they do, what the origin of the concentrations is. There have been numerous charges and countercharges over possible contamination, over the existence of high concentrations of the elements, and over the source of any high concentrations. Despite this, there had not been a thorough study of the situation until now.

The purpose of this study is (1) to establish baseline concentrations of the potentially toxic elements throughout most of the uranium mining area, (2) to determine whether significantly high concentrations exist and, if so, in what settings they exist, and (3) to evaluate different potential mechanisms of pollution--transport of high concentrations of trace elements away from a mining site and resultant contamination of adjacent areas. To accomplish this, systematically collected samples of soil and grass were analyzed for the elements molybdenum, arsenic, selenium, and copper. Although it is not considered environmentally sensitive in this context, copper was also analyzed because molybdenosis is caused by an imbalance between molybdenum and copper.

Since 1975, surface mining of uranium has been regulated, and reclamation of mined areas has been required, by the Texas Surface Mining and Reclamation Law. A further purpose of this study is to provide information to accomplish efficient and effective reclamation. It is hoped that this report can help identify realistic concerns for reclamation, show what potential pollution processes most need to be controlled before reclamation is completed, and evaluate the success of reclamation.

Finally, the significance of different trace elements in animal and human nutrition is poorly understood. By providing information about the natural distribution of elements in soils, this study may aid in deciphering their significance.

SECTION 2

PHYSICAL SETTING

To understand and interpret the origin, distribution, and environmental significance of trace elements in soils, it is necessary to understand (1) the geologic setting--substrate materials are the parent materials of soils, (2) the soils themselves--their nature, origin, and derivation from geologic substrates in a particular climatic setting, and (3) the geochemistry of the elements--how and why they occur in various concentrations in substrates and soils. Exhaustive studies have been made on each of these subjects; no attempt will be made in this report to duplicate these studies, but they will be reviewed as they help to explain the results of this study.

GEOLOGY

The South Texas area, including most of Karnes and Live Oak Counties and parts of Bee and Atascosa Counties, was selected for study because it is the site of uranium mineralization and mining. Here, also, several cases of molybdenosis have been reported and there is concern over the effects of mining in general. Within this area, three geologic formations (fig. 1) are of immediate interest: (1) the Whitsett Formation of the Jackson Group, (2) the Catahoula Formation, and (3) the Oakville Sandstone. The three formations are important because almost all present uranium mining and identified uranium mineralization occurs in them. The uranium and probably other trace elements considered in this study are derived from volcanic ash incorporated in the formations. The mineralization process and the reasons that the elements are concentrated are discussed in the section "Geochemistry of Molybdenum, Arsenic, Selenium, and Copper."

The Whitsett Formation of the Jackson Group consists of interbedded sands and muds deposited in a strandplain-barrier bar system (Fisher and others, 1970). In the western Karnes County area the Whitsett has been subdivided into a lower unit composed of the Dilworth Sandstone and the Conquista Clay Member and an upper unit consisting from oldest to youngest Dewesville Sandstone Member, Dubose Clay Member, Calliham (or Tordillo) Sandstone Member, and the Fashing Clay Member (Barnes, 1976). The sands are dominantly strike oriented, were deposited in a strandplain environment, and are major hosts of uranium ore deposits. The sands are generally 10 to 20 m thick, continue laterally for distances of 50 to 100 km, and extend into the subsurface approximately 15 to 30 km. In many places, including several areas of uranium mineralization, the sands are highly indurated and form resistant ridges.

An aeroradioactivity map (Moxham and Eargle, 1961) shows that radioactivity anomalies are associated with the sands. The greatest radioactivity occurs in western

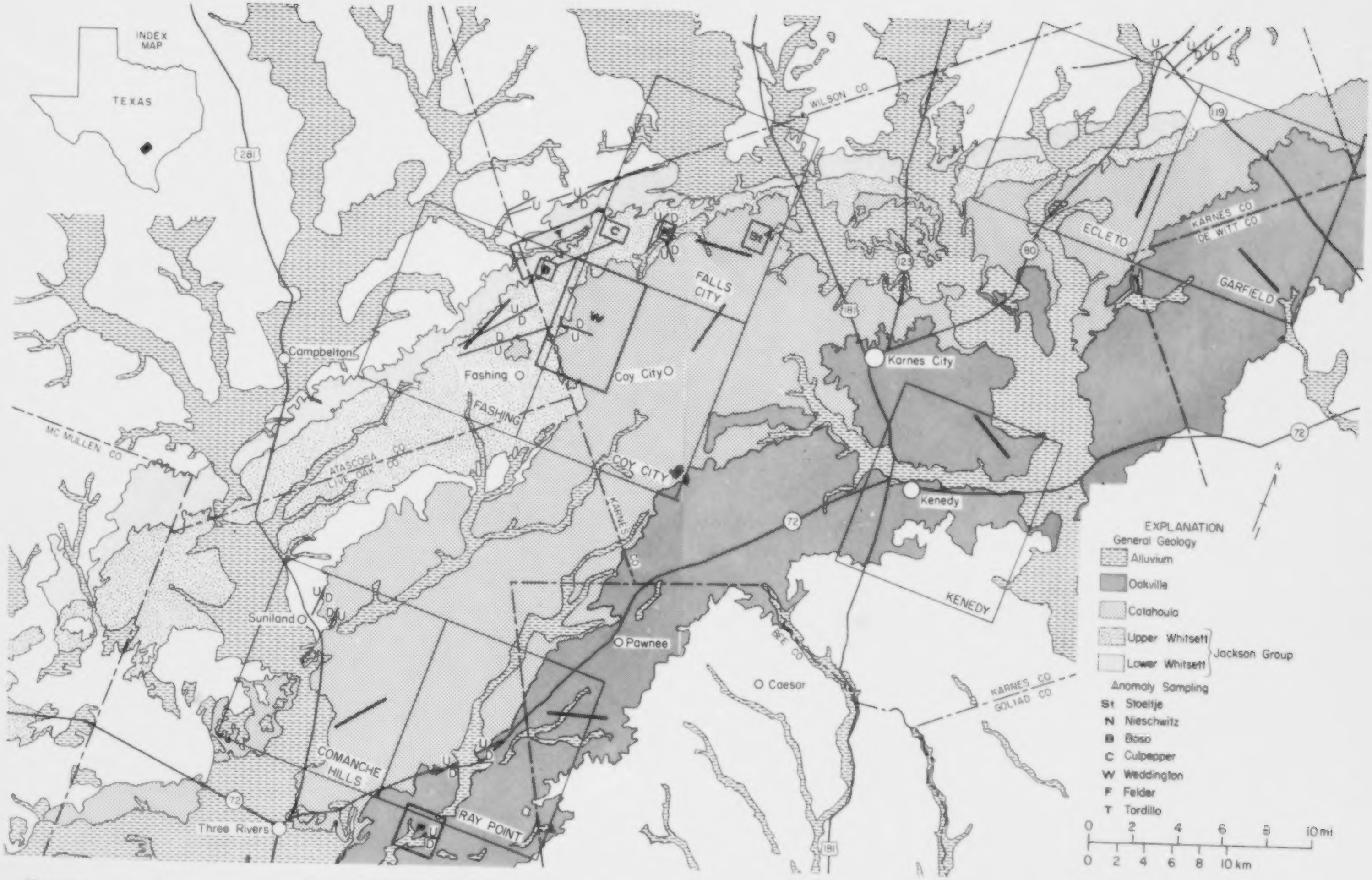
INDEX MAP
TEXAS
281
Campbelton
Fashing
Coy City
FALLS CITY
FASHING
COY CITY
WILSON CO
MC MULLEN CO
ATASCOSA CO
LIVE OAK CO
KARNES CO
Suniland
Three Rivers
COMANCHE HILLS
RAY POINT
Pawnee
Caesar
BEE CO
Karnes City
Kenedy
KENEDY
ECLETO
GARFIELD
KARNES CO
DE WITT CO
GOLIAD CO
72
80
119
123
181
U
D
St
N
B
C
W
F
T
EXPLANATION
General Geology
Alluvium
Oakville
Catahoula
Upper Whitsett
Lower Whitsett
Jackson Group
Anomaly Sampling
St Stoeltje
N Nieschwitz
B Boso
C Culpepper
W Weddington
F Felder
T Tordillo
0 2 4 6 8 10 mi
0 2 4 6 8 10 km

Figure 1. Index map of a part of the South Texas uranium mining district, showing geology and location of background and mining and mineralized area sampling. Large outlined areas are quadrangles of background sampling. Heavy line within each quadrangle is approximate location of sampling barbell.

Karnes County, but anomalies extend at least 60 km both to the northeast and southwest along the outcrop.

Lagoonal or shelf muds (for example, the Dubose Clay) were deposited between the sands. Major dip-oriented, channel sands occur irregularly along the line of outcrop and are also mineralized (White and Galloway, 1977; Fisher and others, 1970).

The Catahoula Formation in the study area (Karnes and Live Oak Counties) consists of interbedded sands and tuffaceous muds deposited in a fluvial environment (Galloway, 1977). A major sediment source, probably a large river system, existed to the southwest, and major fluvial channels diverged from the source. Throughout most of Live Oak and Karnes Counties, the Catahoula outcrop consists of interchannel muds deposited between major channels to the northeast and southwest.

The Oakville Sandstone was also deposited by a major fluvial system, but in the Karnes-Live Oak area the Oakville has a much higher sand content than the Catahoula Formation (W. E. Galloway, unpublished data). The Oakville Sandstone was fed by four major river systems, two of which occur in the Karnes-Live Oak area. Thus, outcrops of the Oakville are mostly sand-rich; a few muddier areas occur in interchannel deposits.

SOILS

The compositions of soils in the study area are strongly influenced by the compositions of the substrates. However, individual soils are not restricted to individual formations because similar substrates commonly occur in different formations. In general, four broad, distinct but overlapping groups of soils correlate with the distinct substrate types. The largest group consists of clay-rich soils developed on muddy parts of the Whitsett Formation, on the mud substrates of the Catahoula Formation, and on the rare, high-mud parts of the Oakville Sandstone. Another group consists of sandy to rocky soils developed on or adjacent to sands and indurated sands of the Whitsett Formation. Soils developed on the nonindurated sands of the Oakville Sandstone are of intermediate to sandy texture. Bottom-land soils developed on Quaternary alluvium constitute a fourth group.

Clayey soils, including the characteristic Monteola clay, Tordia clay, Pawelek clay loam, and Clairville clay loam, are widespread throughout the outcrop area of the Catahoula Formation in Karnes and Live Oak Counties and also form on lagoonal muds of the Whitsett Formation. The soils have low permeability and are alkaline and calcareous; caliche is commonly encountered at depths of 20 to 100 cm. The clay soils are relatively fertile and commonly heavily farmed, being used mostly for cropland or for improved pasture.

Soils developed on the generally indurated sands of the Whitsett Formation include Picosa loam, Weigang silty clay loam, Wilco loamy fine sand, and Cestohowa fine sandy loam. They have a broader range in texture than the clay soils, largely because they are derived from sands interbedded with muds. Rock fragments are common in many of the soils, and in adjacent mud areas the clay-rich soils commonly contain sandstone rock fragments. Other chemical characteristics are also variable and correlate with texture. The pH ranges from less than 7 in sandier soils to 8 or above in the clayier soils; some of the more alkaline soils are calcareous and contain caliche. Much of the area of these soils is moderately rugged (for South Texas) with rock outcrops and slopes up to 25 percent. For these reasons the soils are not heavily cultivated and are used mostly as rangeland.

Soils developed on the nonindurated sands of the Oakville Sandstone are intermediate to sandy textured ranging generally from fine sandy loam to loamy sands. Representative soils are the Runge fine sandy loam, Wilco loamy fine sands, Sarnosa fine sandy loam and Danger clay loam. Upper parts of the sandiest soils are acidic; clayier soils and subsoils of the sandy soils are alkaline and calcareous. The major land use is pastureland. However, much of the area is uncleared rangeland, and some areas are used for crops.

The characteristics of soils in bottom lands along small drainages are largely determined by the composition of soils and substrates in the local drainage area. In the Catahoula Formation most bottom-land soils are alkaline, clay-rich, and poorly drained. Jackson and Oakville bottom-land soils are more variable.

The overall mineralogy of the different soil types is similar, but the soils differ in proportions of the various constituents. In sandy soils, quartz, feldspar, and rock fragments dominate, whereas in fine textured soils, clay minerals are more abundant. Montmorillonite is the dominant clay mineral; illite and kaolinite are common but minor constituents. Calcite as caliche nodules and distinct caliche layers is very common. Clinoptilolite, a zeolite, is a minor constituent in many soils. It is probably derived from the parent rock where it was formed by alteration of volcanic ash.

SECTION 3

GEOCHEMISTRY OF MOLYBDENUM, ARSENIC, SELENIUM, AND COPPER

ASSOCIATION WITH URANIUM IN ORE DEPOSITS

There is a general consensus that the uranium in South Texas ore deposits is derived from volcanic glass incorporated dominantly in the Catahoula Formation, but also in Whitsett Formation and Oakville Sandstone (Galloway, 1977; Eargle and others, 1975). Alteration of the glass by oxidizing, neutral to alkaline ground water released the uranium and transported it to reducing environments where concentration occurred. Uranium is highly soluble in oxidizing, moderate- to high-pH water as a uranyl (UO_2^{++}) ion, especially complexed with carbonate, phosphate, or other anions (Langmuir, 1978). Reduction to insoluble U^{+4} causes precipitation as uraninite (UO_2) or coffinite ($USiO_4$). Reductants that have been cited in South Texas include hydrogen sulfide (H_2S) from sour gas rising along fault zones, pyrite in the sediments (including at least some pyrite derived from the hydrogen sulfide), and carbonaceous material deposited with the sediments (Eargle and Weeks, 1968; Eargle and others, 1975; Goldhaber and Reynolds, 1977). Oxidation of many of the ore fronts has partially remobilized uranium to form uranyl minerals such as uranyl-phosphates (autunite), molybdates (iriginite), silicates (weeksite), or vanadates (carnotite) (Bunker and MacKallor, 1973; Galloway, 1977).

Molybdenum, arsenic, and selenium are geochemically associated with uranium and are concentrated in uranium ore deposits. Molybdenum and arsenic, but possibly not selenium, are enriched in silicic volcanic glass relative to other rocks (Boyle and Jonasson, 1973; Lakin, 1973). Alteration of the glass releases the elements to ground water where they are soluble in oxidizing, neutral to alkaline water as anions ($MoO_4^=$, AsO_4^{3-}, $SeO_3^=$ or $SeO_4^=$). With decreasing Eh, the trace elements are precipitated in a lower valence state commonly as sulfides, as minor constituents of pyrite, or additionally for selenium, as the native element. Molybdenum, arsenic, selenium, and uranium have different oxidation-reduction potentials and may precipitate at different Eh environments (Harshman, 1974). Thus, uranium ore deposits in South Texas are commonly zoned over a narrow but distinct interval with some overlap. Selenium as $SeO_3^=$ reduces to Se at a relatively high Eh, so it occurs towards the updip, oxidized part of the deposits. Molybdenum as $MoO_4^=$ reduces to MoS_2 (molybdenite) at a much lower Eh and occurs farthest downdip in the most reducing environments. Arsenic has an irregular distribution.

The reduced forms can be reoxidized, similar to oxidation of reduced uranium minerals, and as discussed above, can form various uranyl-molybdates or arsenates. Uranyl-selenates or selenites have not been found in South Texas, probably because selenium occurs in low concentration.

Unlike molybdenum, arsenic, selenium, or uranium, copper is soluble in acidic water and insoluble in the moderate or high pH waters in which the other elements are soluble. Copper thus should not be concentrated with uranium or molybdenum, an observation confirmed by Harshman (1974) and Galloway and Kaiser (in press) for uranium deposits in South Texas and elsewhere. Therefore, the concentration of copper in soils of this study is independent of the concentrations of the other elements.

ASSOCIATION IN SOILS

In this study, all analyses have determined the total trace element concentrations. However, trace elements exist in various forms in soil, and not all are equally available to plants. Several studies have pointed out that there is commonly no direct correlation between the total concentration of an element in the soil and its uptake by plants (National Academy of Sciences, 1977a; Williams and Thornton, 1973; Lakin, 1973). Various chemical extraction procedures have been used to determine the availability of elements to plants by comparing amounts of an element obtained from a soil by extraction with the amounts taken up by plants grown on that soil.

Such availability tests have not been used in this study for three reasons:

(1) There is no general agreement on the applicability of various availability tests. For example, the commonly used ammonium oxalate extraction for molybdenum has been applied primarily to acidic soils and may not be applicable to the alkaline calcareous soils of South Texas (I. Thornton, 1977, written communication; Griggs, 1953). EDTA extraction has also been used with moderate success to determine available molybdenum and selenium in relatively acidic soils (Williams and Thornton, 1973). Thornton (1977) recommends measuring total molybdenum content along with various other soil parameters such as pH, organic content, and drainage status. Selenium in water-soluble selenate form is readily available (Lakin, 1973), but selenite may also be available (National Academy of Sciences, 1976).

(2) Soils develop through long time periods, and mature soils are considered to be in equilibrium with their environments. Element partitioning within the soils should remain the same unless the chemical environment of the soil is changed. Seasonal wetting, drying, and temperature changes do occur, but the availability status of an element is unlikely to undergo major change over a brief period. However, many of the samples of this study consist of outcrop material, overburden, or relatively undeveloped soils collected near active or abandoned mines or sites of shallow mineralization. Trace elements in these samples could be contained within sulfides or other forms which are not in equilibrium with the surface environment. Molybdenum (or selenium or arsenic) in these forms is not available to plants and is not determined by most extraction tests. Upon weathering, sulfides will be oxidized and the molybdenum in them will be converted to other forms which may be available to plants. Thus, availability tests, even if they were suited to the soils of South Texas, would be misleading in understanding the potential development of toxic or mineral-deficient soils.

(3) To determine baseline concentrations and to determine whether abnormal concentrations occur as a result of mining or natural processes, it is not sufficient to determine available concentrations of the trace elements.

Major factors that govern availability of molybdenum, arsenic, and selenium are pH and drainage status, although organic content, sulfate content, and other factors may also be significant (Thornton, 1977; Allaway, 1977). Molybdenum will be used as an example, but the following discussion (derived from Barrow, 1977, and Allaway, 1977) is also generally applicable to arsenic and selenium (Lakin, 1973).

The single most important factor in molybdenum availability is pH. Molybdate in soil can exist in three forms: (1) in solution, (2) adsorbed (mostly by iron oxyhydroxides), and (3) firmly bound in resistate minerals (Barrow, 1977). Molybdate in the first two forms is in short-term equilibrium. Below pH 9, iron and aluminum oxyhydroxides have a positive surface charge and can adsorb negatively charged ions such as molybdate (Barrow, 1977). Efficiency of adsorption is pH-dependent: maximum adsorption occurs at pH 4, near the pH of molybdic acid (H_2MoO_4). As pH increases, molybdate adsorption decreases, either because of competition with hydroxide ions for adsorption sites, or because of a decrease in the net positive charge on the oxyhydroxide. Thus, at high pH (high hydroxide concentrations) a large proportion of molybdate is desorbed, in solution, and available to plants.

Drainage status affects molybdenum availability in three ways (Allaway, 1977). (1) Increased soil water content aids transport of dissolved molybdenum to plant roots. (2) Poorly drained soils commonly have low redox potentials. At low redox potentials ferric iron is converted to ferrous iron, and ferrous molybdate is more soluble than ferric molybdate. Also, adsorption may be decreased at lower redox potentials. (3) In sandy, well-drained soils, dissolved molybdenum can be removed by percolation of soil water through the soil and to the water table. In poorly drained soils, dissolved material is removed more slowly.

Copper availability is also affected by pH and drainage status (National Academy of Sciences, 1977b). However, unlike molybdenum, copper is more available at low pH and uptake by plants is severely limited at pH of 6 or above. Like molybdenum, copper is more available in soils with impeded drainage, probably as a result of microbial activity.

In the predominantly alkaline soils of the South Texas uranium mining areas, molybdenum, arsenic, and selenium ought to be relatively more available to plants than copper. This observation is generally confirmed by comparison of copper/molybdenum ratios in soils and grass grown on those soils found in this study, particularly for low swale areas with especially poor drainage. In the sandier soils with lower pH which are characteristically developed on some sands, molybdenum, arsenic, and selenium are probably relatively less available, and copper more available.

Although availability tests have not been made in this study, they would be a useful followup. It would first be necessary to determine what extraction procedures are best applicable to soils of South Texas. This could be done by comparison of extractable concentrations of elements in soils with concentrations of the elements in plants grown on those soils. Bermudagrass, the plant sampled for this study, would be a good choice because it is widely used for forage, but comparison with uptake by other kinds of plants would also be useful.

ENVIRONMENTAL SIGNIFICANCE

Diseases related to trace elements can result from both excesses and deficiencies. What exactly constitutes an excess or deficiency of any element is not well known and depends upon a variety of factors. Excellent reviews of the chemistry, occurrence, and biological significance of molybdenum, arsenic, selenium, and copper exist elsewhere (National Academy of Sciences, 1976, 1977a and 1977b; Luh and others, 1973; Case, 1974; Chappell and Peterson, 1977; Underwood, 1977), and only a few pertinent statements are made here.

The significance of trace element concentrations in food and water is better known than the significance of concentrations in soil but is still not well known. Uptake of molybdenum, arsenic, selenium, and copper by plants depends highly upon the chemical form and availability of the elements and upon the plant species. Herein, total concentrations in soil are considered in a comparative sense along with soil parameters which influence availability.

Molybdenosis is a disease of ruminant animals resulting from ingestion of forage with either high molybdenum or low copper concentrations. Both molybdenum and copper are essential trace elements, but apparently a balance between their concentrations is required for healthy animals. Excess molybdenum can block the metabolism of copper (Case, 1974). Alternatively, cattle ingesting forage with normal molybdenum but low copper concentrations can contract molybdenosis (strictly speaking, a copper deficiency).

Levels of molybdenum and copper in forage that constitute excesses or deficiencies that lead to molybdenosis are not precisely known. Maximum tolerable molybdenum concentrations cited include 10 ppm (W. B. Buck, personal communication, in Dollahite and others, 1972) 5 ppm (Webb and Atkinson, 1965) or even 2 ppm (Thornton, 1977). In fact, Thornton cited examples of molybdenosis or copper deficiency symptoms resulting from ingestion of forage containing from 2 to 10 ppm molybdenum. Copper/molybdenum ratios are also considered important. Buck (Dollahite and others, 1972) suggested that a ratio of 6 or 7 to 1 is considered ideal (see also Case, 1974) whereas a ratio of 2 to 1 is almost certainly too low. Forage with molybdenum concentrations of 2 to 3 ppm and with copper/molybdenum ratios around 5 to 1 were implicated in copper deficiency problems in sheep (Alloway, 1973).

Arsenic is considered essential to animals but not to plants. Poisoning of animals by consumption of arsenic-rich forage seems unlikely because arsenic would significantly reduce plant growth first. Sensitivity of plants to arsenic in soils depends not only upon the chemical form and availability of arsenic but also upon the particular plant species. Available arsenic concentrations as low as 5 to 30 ppm can reduce plant growth as much as 50 percent (National Academy of Sciences, 1977a).

Selenium is essential to plants, livestock, and man, but excesses can be toxic to all three (National Academy of Sciences, 1976). Toxicity to plants depends upon the plant species and the availability of selenium from soil. Certain plants, particularly species of Astragalus, accumulate selenium or are even restricted to selenium-rich soils. Concentrations of selenium toxic to animals can occur in plants grown on soils containing only a few tenths of a ppm water-soluble selenium (Lakin, 1972).

SECTION 4

SOIL SAMPLING

Soil samples collected fall into two general categories: background (random) samples, designed to determine the natural range and scale of variation of concentrations in soils of the uranium mining region; and samples from mining and mineralized areas. Mining and mineralization area sampling is nonrandom and includes sampling areas of shallow mineralization and of mining where anomalous concentrations could be encountered. On the other hand, background sampling is random; the geologic basis, methodology, and statistical model for background sampling are described below.

In this study background concentrations were obtained for two purposes. One purpose is to determine the natural geochemical environment, which is useful in itself, for epidemiological studies, or for agriculture. The other purpose is to provide a baseline with which to compare concentrations in soils in mining and mineralized areas. Both purposes require that the samples collected be representative of the sampled area and show the normal range of concentrations of an element. A critical aspect of the sampling is the use of some procedure to ensure that the samples collected are representative. Characterization usually requires a large number of samples. Thus, the sampling design should be random and allow treatment of the data by statistical tests such as analysis of variance. A variety of sampling designs have been developed in geochemistry (Miesch, 1976). The one used here is generally called stratified random sampling with natural strata.

GEOLOGIC BASIS FOR RANDOM SAMPLING AND SAMPLING METHODOLOGY

The sampling design is divided into a number of levels: the highest level is the South Texas uranium mining region. Within this region, the Whitsett Formation, Catahoula Formation, and Oakville Sandstone, form the first sublevels (fig. 1). All three contain volcanic ash (the source of the uranium) and are the hosts for uranium mineralization. Because the three formations are geologically distinct they may be geochemically distinct also.

It was further desired to test geographic variation within each formation. Thus the uranium mining region was divided into three geographic units; southwestern, central, and northeastern. Within each unit a 7.5-minute quadrangle (fig. 1) was selected to be the second sublevel of sampling. The quadrangles were limited in that one of the formations had to occur within the quadrangle.

It is apparent that there are not three quadrangles for each formation. There are three for the Oakville Sandstone, but four for the Catahoula Formation and only one for the Whitsett Formation. A fourth quadrangle was added to the Catahoula Formation in the central area because much of the uranium mining has occurred in this

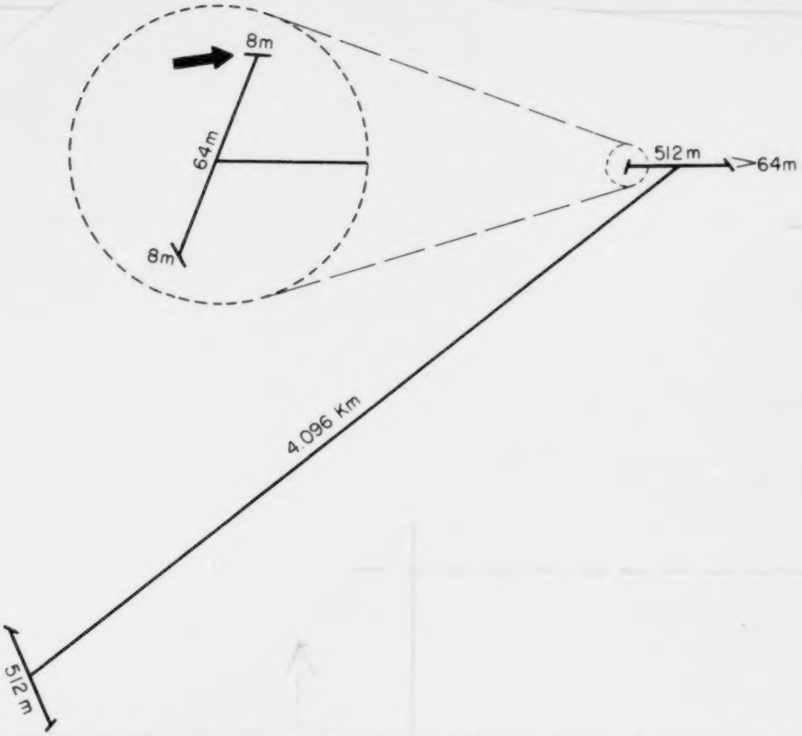

Figure 2. General configuration of the barbell sampling scheme, north to top. The point marked by the arrow is location NE-W-N-W (See also discussion in text). North is toward the top of the figure.

area. Only one quadrangle was selected in the Whitsett Formation because it has a narrow outcrop and only in the central area is the outcrop wide enough for the barbell sampling design.

Variations in trace element concentrations at different scales (Miesch, 1976) were determined within each quadrangle by a barbell sampling design (fig. 2). Each barbell is constructed by randomly selecting a point and a direction (derived from random number tables). The point is used as the midpoint of a line 4.096 km long and in the selected direction. The end points of this line define the midpoints of two new lines with randomly selected directions. This process is repeated three times with lines 512 m, 64 m, and 8 m long. The end points of the 8-m lines are sampling locations.

At each location samples were collected from the A and B soil horizons. Thus there are a total of 16 locations and 32 soil samples from each quadrangle. Barbells were constrained so that all sample locations fall within the formation of interest. If any points were not in the formation, the entire procedure was repeated until all sample points were in the formation.

Each sampling location is uniquely defined by a quadrangle name and set of directions. Thus (Quadrangle) NE-W-N-W A is the location marked by the arrow on figure 2. The directions were selected and measured in the field to the nearest degree but have been abbreviated in the sample designation. For example, N25°E would be NE. The final A in the sample designation indicates that it is from the A horizon. The set of samples from a quadrangle is identified by geologic formation and quadrangle; for example, Catahoula (Coy City).

Soil samples were collected at each location with a soil auger. A horizon samples are from 0 to 20 cm deep and B horizon samples from 40 to 60 cm deep. These depths do not exactly correspond with identified soil boundaries, but they are consistent with soil profiles described by the Soil Conservation Services of the United States Department of Agriculture. At a few locations an impenetrable caliche layer was encountered at a depth less than 60 cm. At these locations the B horizon sample was taken at whatever depth could be reached. Contamination of B horizon samples by A horizon samples was not a problem because soils of this study are generally coherent and do not tend to collapse into the auger hole.

Bermudagrass was collected from eight locations in the random sampling. The grass samples are identified by the same terminology as was used for the soil samples at the same location with the additional notation that they are Bermudagrass.

Ideally background samples should be taken before mining occurs. This is impossible for the overall uranium district although it can be done for individual mine sites. Thus it is at least remotely possible that any sample has been affected by uranium mining. However, the mines are concentrated in a few areas, and it is highly unlikely that contamination has occurred over such a wide area that background concentrations cannot be obtained.

SAMPLING IN AREAS OF MINING AND MINERALIZATION

Samples in areas of mining or shallow mineralization were collected nonrandomly from specific locations to test hypothesized processes or concepts. Thus samples were collected upwind and downwind of mining areas to determine if wind transport of exposed ore or overburden could affect molybdenum or other trace element concentrations in soils adjacent to the mining area. In areas of suspected or identified shallow mineralization, sample traverses were made across the mineralized zone. Where erosion of spoil piles had broken down former protective berms, samples were taken of the eroded material and in drainages downstream. Most of the sampled drainages are broad, low swales without sharply defined channels. Where the drainages are within pastures, the entire area is commonly planted with grass such as Bermudagrass. For convenience and clarity, soil samples collected within the area inundated by stream flow are referred to as samples within the channel; samples collected outside the inundated area but within the drainage area are referred to as samples within the drainage area. To evaluate water-borne transport requires identifying and sampling appropriate channels.

Evaluation of wind transport requires knowledge of wind patterns. During most of the year, winds from the south-southeast (from the Gulf of Mexico) prevail in the region (Arbingast and others, 1973). During a few winter months, there is a minor northerly component introduced by "northers," cold fronts moving from north to south. However, the northers do not dominate the winter wind pattern in the way that the coastal breezes prevail the rest of the year.

South-southeast winds are most important for possible wind transport for another reason. During the dry, summer months, the ground is dry and loose, especially on unreclaimed spoil piles, and readily disturbed by wind. During the wet winter months, soil and overburden are much less susceptible to wind erosion. Thus dominant wind transport should be from the south-southeast towards the north-northwest. Sampling patterns to evaluate wind transport were thus designed accordingly.

At most locations both A and B horizons (as defined for the random sampling) were sampled. In several places a sample of grass was also collected. In some locations it was possible or necessary to sample only the A horizon. For example, only the A horizon was collected from some thin soils developed on shallow bedrock. At a particular sampling location anywhere from 1 to 3 samples of soil and grass were collected.

SAMPLING DESIGN AND STATISTICAL MODEL

Depending upon the nature and purpose of investigation, different statistical models define various sampling designs. A nested or hierarchical model is quite common in geochemical sampling where the levels for a given factor are all different across the levels of the other factors. Frequently the levels are chosen at random for each factor in which case it is called a "random nested design." Nested design is also known as multistage sampling. The other types of designs include fixed models and mixed models.

The problem at hand involves a sampling design known as stratified random sampling. In simple random sampling, a number of sampling points can be selected at random in a given region for geochemical analysis. Stratified random sampling is more suitable wherever the population (entire region to be sampled) can be divided into subpopulations which are uniform in the characteristics to be studied. In the present study the entire region is divided into three subpopulations, the three geologic formations, and these three geological units are further subdivided into 7½-minute quadrangles. The barbell type of sampling design described in the previous section is used within each quadrangle. This type of multistage sampling design where the factors are nested within other factors is known as nested or hierarchical design. There can be two or more levels for each factor or sampling level. As many sampling levels can be included in the nested sampling design as desired. Usually the highest sampling levels designate the largest unit to be sampled (the South Texas uranium mining region in this case). The sublevels are nested within these levels successively until the smallest desirable sampling unit (or distance) is obtained. Levels used in this study are 4.096 km, 512 m, 64 m, 8 m, and A and B soil horizons.

The statistical model for the sampling design can be described as:

$$Y_{ijklmnop} = \mu + \alpha_i + \beta_{(i)j} + \gamma_{(ij)k} + \delta_{(ijk)l} + \rho_{(ijkl)m} + \eta_{(ijklm)n} + \lambda_{(ijklmn)o} \; \varepsilon_{(ijklmno)p}$$

where μ = grand mean of the entire region

α = deviation related to different geological units

β = deviation related to quadrangles within each unit

γ = deviation related to 4.096-km links within each quadrangle

δ = 512-m links within each 4.096-km link

ρ = 64-m links within each 512-m link

η = 8-m links within each 64-m link

λ = A and B horizons within 8-m links

ε = unexplained error

and $Y_{ijklmnop}$ is an individual value.

The total variance associated with 256 analytical values (the total number of random samples; 8 quadrangles multipled by 32 samples per quadrangle) is the sum of individual variance components as described by:

$$\sigma_y^2 = \sigma_\alpha^2 + \sigma_\beta^2 + \sigma_\gamma^2 + \sigma_\delta^2 + \sigma_\rho^2 + \sigma_\eta^2 + \sigma_\lambda^2 + \sigma_\varepsilon^2$$

In estimating variance components, an appropriate analysis of variance procedure is used. However, such an analysis of variance method can be applied only on data that are normally distributed. Trace elements tend to occur in lognormal distribution in nature and therefore a lognormal transformation of raw data was necessary before analysis of variance procedure could be used.

The description of the barbell sampling shows that the level of any factor such as a 512-m link cannot be same as the levels of the factor, 4.096-km link. Because there are never the same 512-m links within the various 4.096-km links, it is impossible to obtain an interaction between them. This concept of not being able to obtain an interaction is always present in a nested design.

In the statistical model discussed above,

i = 1, 2,....a
j = 1, 2,....b
k = 1, 2,....c
l = 1, 2,....d
m = 1, 2,....e
n = 1, 2,....f
o = 1, 2,....g
p = 1, 2,....h

The analysis of variance, which contains the source of variation, the degrees of freedom for each source, sum of squares of variances, mean squares, and F-ratios, is presented in Table 1.

TABLE 1: ANOVA (ANALYSIS OF VARIANCE)

Source	Degrees of freedom	Sum of squares	Mean square	F-ratio
Geological units within the region	a-1	SS_1	$V_1 = SS_1/a-1$	V_1/V_2
Quadrangles within the Geological units	a(b-1)	SS_2	$V_2 = SS_2/a(b-1)$	V_2/V_3
4.096-km links within the quadrangles	ab(c-1)	SS_3	$V_3 = SS_3/ab(c-1)$	V_3/V_4
512-m links within the 4.096 km links	abc(d-1)	SS_4	$V_4 = SS_4/abc(d-1)$	V_4/V_5
64-m links within the 512-m links	abcd(e-1)	SS_5	$V_5 = SS_5/abcd(e-1)$	V_5/V_6
8-m links within the 64-m links	abcde(f-1)	SS_6	$V_6 = SS_6/abcde(f-1)$	V_6/V_7
A and B horizons within the 8-m links	abcdef(g-1)	SS_7	$V_7 = SS_7/abcdef(g-1)$	V_7/V_8
Unexplained error	abcdefg(h-1)	SS_8	$V_8 = SS_8/abcdefg(h-1)$	

In Table 1 the number of levels is constant in the subclasses. In the actual sampling design, the number of levels was different. Table 2 displays the procedure used in estimating the overall variance components.

TABLE 2: ESTIMATION OF VARIANCE COMPONENTS

Levels	Difference in mean squares	Sample size	Variance components
Geological units	$V_1 - V_2$	bcdefgh	$\sigma_\alpha^2 = (V_1 - V_2)/bcdefgh$
Quadrangles	$V_2 - V_3$	cdefgh	$\sigma_\beta^2 = (V_2 - V_3)/cdefgh$
4.096-km links	$V_3 - V_4$	defgh	$\sigma_\gamma^2 = (V_3 - V_4)/defgh$
512-m links	$V_4 - V_5$	efgh	$\sigma_\delta^2 = (V_4 - V_5)/efgh$
64-m links	$V_5 - V_6$	fgh	$\sigma_\rho^2 = (V_5 - V_6)/fgh$
8-m links	$V_6 - V_7$	gh	$\sigma_\eta^2 = (V_6 - V_7)/gh$
A and B horizons	$V_7 - V_8$	h	$\sigma_\lambda^2 = (V_7 - V_8)/h$
Unexplained error	V_8	1	$\sigma_\varepsilon^2 = V_8$

where $\sigma_\alpha^2, \sigma_\beta^2 \ldots\ldots, \sigma_\varepsilon^2$ are defined above.

For the present experimental design, no replicate analyses were done. An overall analysis of variance was performed using the RASS-STATPAC program developed by the U.S. Geological Survey, because the first two factors (namely geological units and quadrangles) have an unequal number of levels within them. This program is based on the method described in Anderson and Bancroft (1952).

A special program was developed at the Bureau of Economic Geology to compute variance components and to perform the analysis of variance tests on an individual quadrangle where all the factors and subclasses of factors were equal in number (table 3). The tests were repeated for four different trace elements, and the discussion of results obtained is presented in the following section.

TABLE 3: ANALYSIS OF VARIANCE FOR INDIVIDUAL QUADRANGLES

Source	Degrees of freedom	Sum of squares	Mean square	Expected mean square
4.096 km (γ)	1	SS_γ	V_γ	$\sigma_\lambda^2 + \lambda\eta\sigma_\rho^2 + \lambda\eta\rho\sigma_\delta^2 + \lambda\eta\rho\delta\sigma_\gamma^2$
512 m (δ)	2	SS_δ	V_δ	$\sigma_\lambda^2 + \lambda\sigma_\eta^2 + \lambda\eta\sigma_\rho^2 + \lambda\eta\rho\sigma_\delta^2$
64 m (ρ)	4	SS_ρ	V_ρ	$\sigma_\lambda^2 + \lambda\sigma_\eta^2 + \lambda\eta\sigma_\rho^2$
8 m (η)	8	SS_η	V_η	$\sigma_\lambda^2 + \lambda\sigma_\eta^2$
A and B horizons (λ)	16	SS_λ	V_λ	σ_λ^2

where λ, η, ρ, δ, and γ are the number of levels at factors A and B horizon, 8 m, 64 m, 512 m, and 4.096 km, respectively.

All factors have equal numbers of levels (two) and the following relationship exists by equating the fourth and the last columns of table 3. Because theoretically the expected mean square should be equal to the mean square,

$$V_\lambda = \sigma_\lambda^2 + 2\sigma_\eta^2 + 4\sigma_\rho^2 + 8\sigma_\delta^2 + 16\sigma_\lambda^2$$

$$V_\delta = \sigma_\lambda^2 + 2\sigma_\eta^2 + 4\sigma_\rho^2 + 8\sigma_\delta^2$$

$$V_\rho = \sigma_\lambda^2 + 2\sigma_\eta^2 + 4\sigma_\rho^2$$

$$V_\eta = \sigma_\lambda^2 + 2\sigma_\eta^2$$

$$V_\lambda = \sigma_\lambda^2$$

From the above set of equations, we obtain:

$$\sigma_\lambda^2 = (V_\lambda - V_\rho)/16$$

$$\sigma_\delta^2 = (V_\delta - V_\rho)/8$$

$$\sigma_\rho^2 = (V_\rho - V_\eta)/4$$

$$\sigma_\eta^2 = (V_\eta - V_\lambda)/2$$

$$\sigma_\lambda^2 = V_\lambda$$

Analysis of variance indicates at what scale variations in the trace element concentrations occur. For example, if most variance occurs at the higher levels with very little at lower levels, soils are regionally homogeneous. Widely spaced samples could be used to describe the trace element variation. However, if a major part of the variance is at lower levels, the soils are heterogeneous. Samples would have to be collected from closely spaced intervals to depict the variation in trace element concentration accurately.

SECTION 5

RESULTS OF RANDOM SAMPLING

Table 4 summarizes basic statistics of the analyses from the random sampling program; the results are tabulated by formation and quadrangle. All analytical results are given in Appendix A, Table A-1. Results of analysis of variance are given in Table A-3.

STATISTICAL INTERPRETATION

Multiple comparisons of the means of the elements from the various formations and quadrangles were made by the Newman-Keuls test (Table 5). The tests show whether or not the means were significantly different. For all tests a level of significance of 0.05 was used.

Analysis of variance (ANOVA) shows that within each quadrangle of all three formations a major part of the variance is at the lowest level, between the A and B horizon samples. Variance due to unexplained error is included at this level. The percentage of variance at the lowest level ranges from 19 percent (Catahoula-Ecleto) to 70 percent (Catahoula-Comanche Hills). Very little of the variance occurs at the highest level, between sample groups 4.096 km apart. Only the Oakville (Ray Point) samples have very much of the variance, 38 percent, at the highest level. For all other quadrangles variance at this level comprises no more than 3 percent of the total.

Most variance which is not at the lowest level is at intermediate distance levels, and mostly at 512 m or 64 m. For example, all the variance in the Whitsett (Fashing) samples is at the lowest level (44 percent) or the 512 m level (56 percent). Variance at the 512 m level is significant at the 0.01 probability level. Other quadrangles have roughly similar patterns.

In general, similar patterns exist for selenium, copper, and arsenic results. Most variance is at the lowest level, most of the rest is at an intermediate distance level, and variance at the highest level is very low with only a few exceptions.

The ANOVA results show that the soils are inhomogeneous in their trace element concentrations at intermediate distance levels. Thus, to construct a geochemical map with high resolution (as defined by Miesch, 1976) samples would have to be more closely spaced than the intermediate distance levels, even ignoring the variation between A and B horizons. To do so would be time consuming and would not add measurably to an understanding of trace element distributions. For example, if samples needed to be collected at a 200-m interval, a 1 km^2 area would require 50 samples (a 5 x 5 grid with A and B horizons samples at each grid point). An area the

TABLE 4. SUMMARY OF BASIC STATISTICS
All concentrations in ppm

Formation Quadrangle	Range	Means Arithmetic	 Geometric	Variance	Standard Deviation	Upper Limit for Expected Range	No. of Outliers
			MOLYBDENUM				
Whitsett							
Fashing	0.2 - 4.6	2.1	1.8	0.86	0.93	6.05	0
Catahoula							
Ecleto	0.3 - 4.0	1.1	0.95	0.56	0.75	3.19	1
Falls City	0.2 - 1.0	0.69	0.66	0.039	0.20	1.33	0
Coy City	0.5 - 1.6	0.99	0.97	0.046	0.22	1.60	1
Comanche Hills	0.4 - 1.4	0.73	0.71	0.026	0.16	1.10	1
Oakville							
Garfield	0.4 - 1.3	0.84	0.80	0.066	0.26	1.53	0
Kenedy	0.5 - 1.2	0.82	0.80	0.043	0.21	1.34	0
Ray Point	0.3 - 2.0	0.91	0.84	0.146	0.38	1.89	1
			SELENIUM				
Whitsett							
Fashing	0.01- 0.90	0.18	0.10	0.038	0.20	1.10	0
Catahoula							
Ecleto	0.03- 0.60	0.15	0.117	0.019	0.14	0.47	2
Falls City	0.01- 0.30	0.18	0.16	0.005	0.07	0.53	0
Coy City	0.01- 0.31	0.07	0.04	0.004	0.07	0.32	0
Comanche Hills	0.02- 0.26	0.13	0.117	0.0026	0.05	0.32	0
Oakville							
Garfield	0.10- 0.30	0.19	0.19	0.003	0.05	0.32	0
Kenedy	0.01- 0.38	0.14	0.09	0.010	0.10	0.87	0
Ray Point	0.09- 0.37	0.19	0.18	0.003	0.05	0.32	1

(continued)

TABLE 4. (continued)

Formation Quadrangle	Range	Means Arithmetic	Means Geometric	Variance	Standard Deviation	Upper Limit for Expected Range	No. of Outliers
			COPPER				
Whitsett							
Fashing	3.4 - 8.3	5.5	5.4	1.6	1.3	8.39	0
Catahoula							
Ecleto	2.9 - 20	8.0	7.9	9.2	3.0	14.0	1
Coy City	4.2 - 12	8.6	8.4	4.0	2.0	13.8	0
Comanche Hills	6.1 - 13	10.8	10.7	2.1	1.4	14.0	0
Oakville							
Ray Point	7.9 - 13	10.1	10.0	2.0	1.4	13.1	0
			ARSENIC				
Whitsett							
Fashing	0.6 - 17	5.3	4.6	8.2	2.9	13.8	1
Catahoula							
Coy City	0.2 - 6.9	3.4	2.7	3.2	1.8	12.7	0

TABLE 5. NEWMAN-KEULS MULTIPLE COMPARISON TESTS

α = 0.05
S = Significant
NS = Not Significant

Mo

	Whitsett (Fashing)	Catahoula (Ecleto)	Catahoula (Falls City)	Catahoula (Coy City)	Catahoula (Comanche Hills)	Oakville (Oakfield)	Oakville (Kenedy)
Whitsett (Fashing)							
Catahoula (Ecleto)	S						
Catahoula (Falls City)	S	S					
Catahoula (Coy City)	S	NS	S				
Catahoula (Comanche Hills)	S	S	NS	S			
Oakville (Oakfield)	S	S	NS	NS	NS		
Oakville (Kenedy)	S	S	NS	NS	NS	NS	
Oakville (Ray Point)	S	NS	NS	NS	NS	NS	NS

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TABLE 5. (continued)

Se

	Whitsett (Fashing)	Catahoula (Ecleto)	Catahoula (Falls City)	Catahoula (Coy City)	Catahoula (Comanche Hills)	Oakville (Oakfield)	Oakville (Kenedy)
Whitsett (Fashing)							
Catahoula (Ecleto)	NS						
Catahoula (Falls City)	NS	NS					
Catahoula (Coy City)	S	S	S				
Catahoula (Comanche Hills)	NS	NS	NS	S			
Oakville (Oakfield)	NS	NS	NS	S	NS		
Oakville (Kenedy)	NS	NS	NS	S	NS	NS	
Oakville (Ray Point)	NS	NS	NS	S	NS	NS	NS

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TABLE 5. (continued)

Cu

	Whitsett (Fashing)	Catahoula (Ecleto)	Catahoula (Coy City)	Catahoula (Comanche Hills)
Whitsett (Fashing)				
Catahoula (Ecleto)	S			
Catahoula (Coy City)	S	NS		
Catahoula (Comanche Hills)	S	S	S	
Oakville (Ray Point)	S	S	S	NS

As

	Whitsett (Fashing)	Catahoula (Coy City)
Whitsett (Fashing)		
Catahoula (Coy City)	S	

size of a quadrangle (150 km^2) would require 7,500 samples. Such a sampling program is unrealistic.

We have used the procedure of Tidball and others (1974) to establish a geochemical baseline. They designated an "expected range" as the central 95 percent range of concentrations assuming lognormal distribution. Only one concentration in 20 should fall outside the central 95 percent range and only one in 40 should lie above the range. Because this study is concerned primarily with anomalously high concentrations, we have provided only the upper limit of the expected range (Table 4). Because almost all variance occurs at scales less than 4.096 km, the upper limit for a quadrangle should be applicable throughout the area of the quadrangle.

CORRELATION WITH GEOLOGY

Several conclusions come from relating the analytical results to geology. First, the different geologic formations have different trace element concentrations (Tables 4 and 5). This pattern is most obvious for molybdenum. The Whitsett (Fashing) samples contain the highest molybdenum concentrations and have the highest variance--they have the greatest range of molybdenum concentrations of the various formations. Because the Whitsett Formation was sampled only in the Fashing Quadrangle, which includes areas of shallow mineralization and anomalous radioactivity, characterization beyond the boundaries of the quadrangle is unwarranted.

The Catahoula Formation and Oakville Sandstone have lower concentrations and are geographically uniform; there is not a regional pattern to the concentrations. The Oakville Sandstone is particularly homogeneous with very similar means (0.82 - 0.91 ppm) and ranges from each quadrangle. The Catahoula Formation is also relatively homogeneous, but the Catahoula (Ecleto) samples (the northeasternmost quadrangle sampled) have slightly higher means and higher variance than other Catahoula samples, reflecting a few distinctly higher molybdenum concentrations.

The low concentrations of trace elements in the Catahoula Formation and Oakville Sandstone and the higher concentrations in the Whitsett Formation imply that different geologic processes have acted on each to create the pattern of concentrations. Volcanic ash incorporated in the three formations was the source for molybdenum, arsenic, and selenium, along with the uranium. Galloway and Kaiser (in press) showed that the volcanic material had been efficiently depleted of uranium and that soil-forming processes were particularly effective in removing uranium. Although Galloway and Kaiser were referring to soil formation that occurred during original deposition of the Catahoula, the implication is that molybdenum was also depleted at that time. Thus the Catahoula substrate in the area of this study was depleted of molybdenum early in its history and soils presently forming on the substrate are low in molybdenum. A similar process probably explains the low and uniform molybdenum concentrations of the Oakville Sandstone.

Molybdenum concentrations in the Whitsett Formation must have a more complicated origin. Two lines of evidence are critical in understanding their origin: (1) the spatial distribution of concentrations within the Whitsett (Fashing) samples, and (2) the distribution and intensity of radioactivity determined from airborne surveys (Moxham and Eargle, 1961).

The Whitsett (Fashing) samples can be considered as four groups, one each at the end of the 512-m lines. Three groups (N-NW, S-SE, S-NW; table A-1) have high concentrations (1.5 to 4.6 ppm) whereas one group (N-SE) has low concentrations (0.2 - 1.9 ppm) more like those of the Catahoula samples than like the other Whitsett (Fashing) samples. There are distinct geochemical subenvironments within the Whitsett Formation as there are distinct geological subenvironments. The geological subenvironments are the barrier bar sands and the lagoonal muds. The high concentrations are associated with the sands and, as is shown below, are due to mineralization of the sands.

Correlation of high concentrations and sands is not obvious from inspection of the soil types of the Whitsett Formation (table A-1). The high concentrations are found in clays and silty clay loams, and the low concentrations are in clays. However, geologic maps (Eargle and others, 1961) show that the three groups with high concentrations were taken within or near the outcrop of sands of the Whitsett. For example, sandstone crops out near the S-NW set of samples and sandstone fragments are common in the clay soil there. The low concentration group (N-SE) on the other hand is developed on the Dubose Clay Member of the Whitsett and is not near any areas of sandstone outcrop. The pattern of soil pH also reflects the different parentage. Soil pH (although variable) is generally low on the sand-related, high molybdenum concentration soils and higher on the low concentration soils.

Higher molybdenum concentrations are associated with the sands because they are mineralized. As discussed previously, uranium deposits are formed by reduction of oxidizing, uranium-rich ground water. Uranium mineralization crops out in some of the Whitsett sands although most mineralization occurs in the sands at a variable distance downdip from outcrop. However, the mineralizing fluid passed through the sands updip of the uranium deposits, resulting in minor mineralization at the contact of the sand with enclosing muds. The contact is mineralized because the muds are reduced. Most mineralization is minor and not of economic consequence but along with the uranium would leave a geochemical halo of trace elements including molybdenum. It is this halo, then, that is creating the higher concentration of molybdenum in Whitsett soils. Formation of the present soils partially disperses the mineralization halo, so high concentrations are probably irregularly distributed around the sands and overlap into areas of clay outcrop. Recognition of this kind of process and identification of mineralization halos is a basic method of geochemical exploration.

Radioactivity anomalies are another indication of this mineralization. Figure 3 shows the distribution of radioactivity in the area of study determined by Moxham and Eargle (1961). The highest radioactivity (more than 770 counts per second) identifies small areas of intense, shallow mineralization including minable (and mined) deposits. Radioactivity at some of these locations is as high as 5,000 μr/hr (MacKallor and others, 1962). Molybdenum concentrations in natural soils at these locations are extremely high (several tens of ppm - see section, Results of Mining and Mineralized Area Studies). In addition to these small areas of intense radioactivity, there are broad areas of moderately high radioactivity which mark areas of minor mineralization. The Whitsett (Fashing) samples were collected within an area of moderate radioactivity.

The moderately high concentrations of molybdenum (several ppm) do not result from widespread dispersion from the areas of intense, shallow mineralization. Disper-

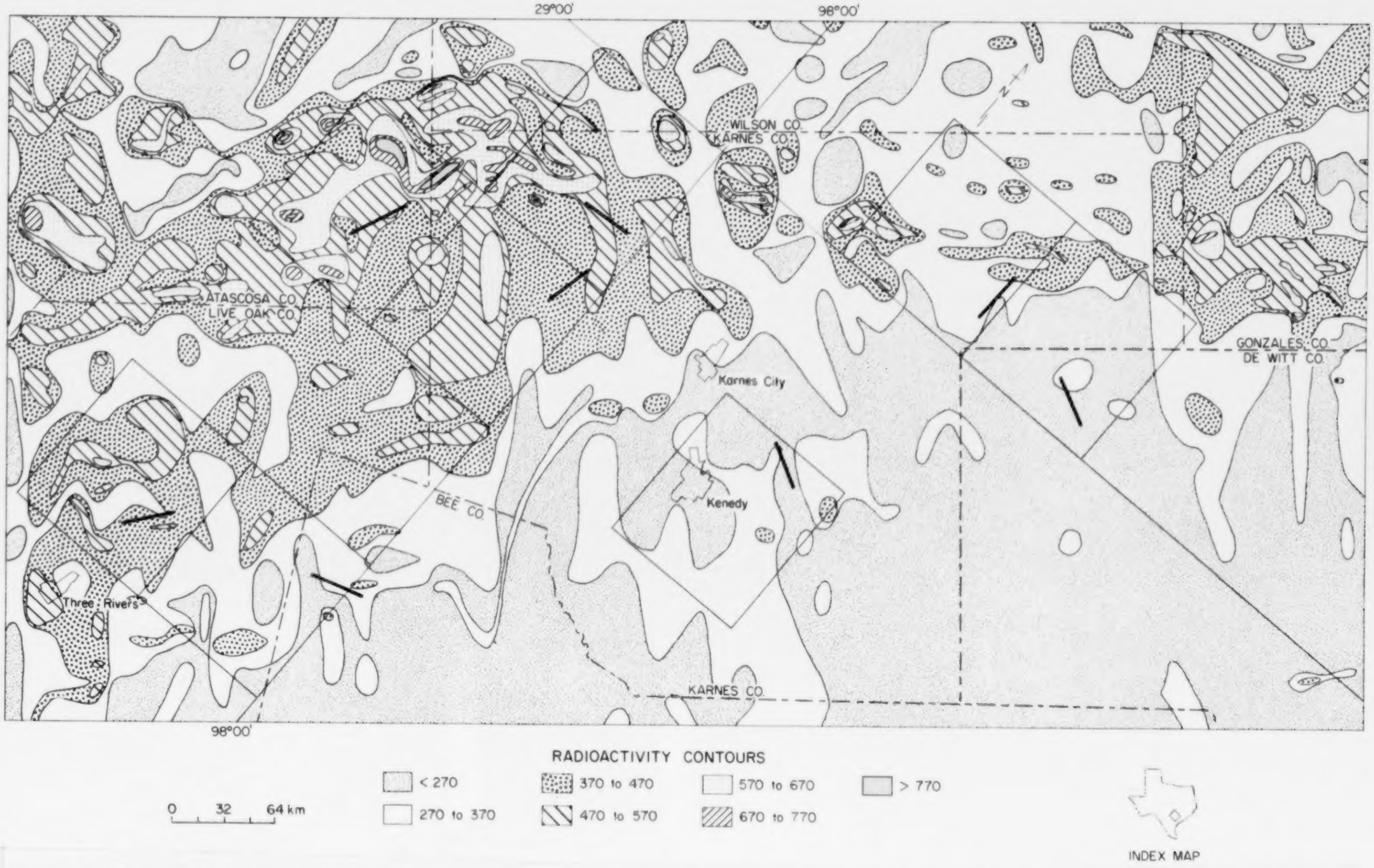
29°00'
98°00'
WILSON CO.
KARNES CO.
ATASCOSA CO.
LIVE OAK CO.
GONZALES CO.
DE WITT CO.
Karnes City
Kenedy
BEE CO.
Three Rivers
KARNES CO.
98°00'
N
RADIOACTIVITY CONTOURS
< 270
270 to 370
370 to 470
470 to 570
570 to 670
670 to 770
> 770
0 32 64 km
INDEX MAP

Figure 3. Map of aeroradioactivity (in counts per second measured at an approximate altitude of 150 m) of part of the South Texas uranium mining district (adapted from Moxham and Eargle, 1961). Quadrangle areas and locations of barbell sampling are the same as appear in figure 1.

sion over distances of several kilometers is obviously unlikely and even if dispersion had occurred, it would produce a halo with no relationship to local substrate conditions. The fact that molybdenum concentrations in Whitsett (Fashing) samples vary with soil and substrate composition shows that widespread dispersion is not occurring; Moxham (1964) reached a similar conclusion.

An implication of the mineralization halos and radioactivity anomalies (fig. 3) is that moderately high concentrations of trace elements should occur commonly throughout the Whitsett Formation and possibly in some other formations. Unfortunately, radioactivity is not a perfect indicator of high molybdenum concentration. Not only do other elements (potassium and thorium) besides uranium contribute to radioactivity but also molybdenum and the other trace elements are not concentrated proportionately with uranium. For example, radioactivity in the area of the Catahoula (Falls City) and Catahoula (Coy City) samples is nearly as high as in the area of the Whitsett (Fashing) samples (figure 3). However, molybdenum concentrations of the Catahoula samples are much lower than concentrations in the Whitsett samples. Radioactivity can only be used as a qualitative indicator of areas that should be examined more carefully.

Although not found in this study, high concentrations of molybdenum could exist in the Catahoula Formation or Oakville Sandstone. Shallow mineralization actually occurs in the Oakville Sandstone at the Felder Site (see section, Results of Mining and Mineralized Area Studies) and moderate radioactivity occurs in both formations in several areas (fig. 3). The part of Catahoula Formation sampled in this study is largely within a major interchannel area with sparse mineralization (fig. 4) (Galloway, 1977). Mineralization in the Catahoula Formation is dominantly within channel sands to the southwest. Shallow mineralization is not known from that area but if it occurs, soils in the area could have high molybdenum concentrations. In any event, the types of areas that could have naturally high concentrations are generically similar in all formations.

Selenium shows a similar, but less pronounced, pattern to molybdenum (table A-1). The Whitsett (Fashing) samples do not, however, have the highest mean selenium concentration. They do have the highest individual selenium concentrations (up to 0.9 ppm), the greatest variance, and the greatest upper limit for the expected range (1.1 ppm). This indicates that parts of the Whitsett Formation are enriched in selenium and parts are not, similarly to molybdenum.

Selenium concentrations in the Catahoula Formation and Oakville Sandstone are more uniform and again do not show a regional pattern (Tables 4 and 5). The highest variance of any of the Catahoula and Oakville samples is shown by the Ecleto quadrangle samples, which also have the highest variance for molybdenum.

Arsenic was analyzed for only two quadrangles, and too little data exist to make any major conclusions. Nevertheless, Whitsett (Fashing) samples have greater arsenic concentrations than Catahoula (Coy City) samples (Tables 4 and 5). This relationship generally agrees with the molybdenum and selenium patterns.

Copper, analyzed for five quadrangles, shows the reverse pattern (Tables 4 and 5). Whitsett samples have the lowest copper concentrations. Concentrations in three Catahoula quadrangle samples are higher and relatively uniform although there is a slight suggestion of a regional pattern with higher concentrations to the southwest.

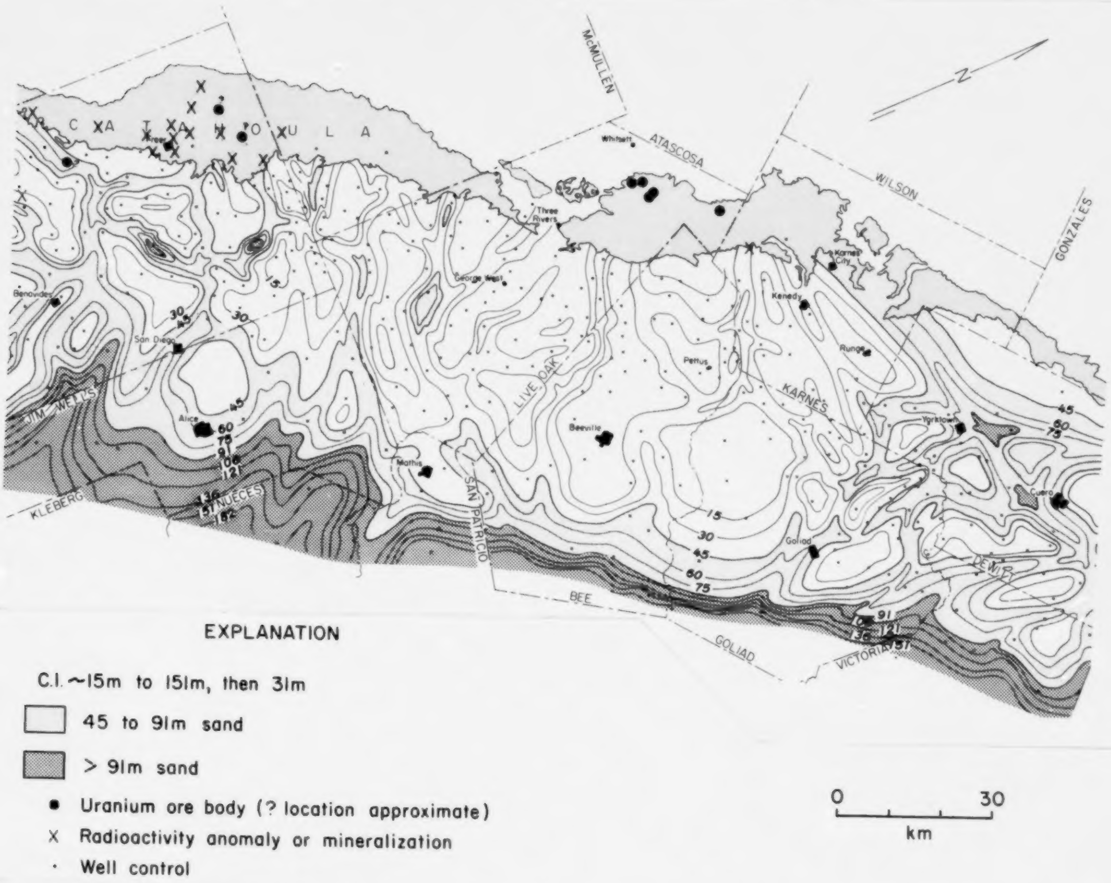
N
CATAHOULA
McMULLEN
ATASCOSA
WILSON
GONZALES
LIVE OAK
KARNES
JIM WELLS
KLEBERG
NUECES
SAN PATRICIO
BEE
GOLIAD
VICTORIA
DEWITT
Benavides
San Diego
Alice
Mathis
George West
Three Rivers
Whitsett
Pettus
Beeville
Kenedy
Karnes City
Runge
Yorktown
Cuero
Goliad
15
30
45
60
75
91
106
121
136
151
EXPLANATION
C.I. ~15m to 151m, then 31m
45 to 91m sand
> 91m sand
Uranium ore body (? location approximate)
Radioactivity anomaly or mineralization
Well control
0
30
km

Figure 4. Map of Catahoula Formation outcrop and net sand in subsurface. Adapted from Galloway (1977).

Concentrations in Oakville (Ray Point) samples are very similar in mean and variance to concentrations in samples from the adjacent Catahoula (Comanche Hills) samples.

Within each quadrangle there is very little correlation between the different elements (table A-4). Clearly, copper should not correlate with molybdenum, arsenic, or selenium because of the difference in their chemical properties and behavior in mineralization and in soils. However, better correlation might be expected between molybdenum, arsenic, and selenium. Only molybdenum and selenium in the Whitsett (Fashing) samples correlate moderately well (R = 0.61). The correlation is additional evidence that uranium mineralization is responsible for the higher concentrations in Whitsett samples. The mineralization process concentrates both elements so samples enriched in one element are enriched in the other. The correlation is not perfect probably because mineralization does not concentrate them exactly together and because soil formation partially disperses them.

The purpose of the random sampling program was to establish baseline concentrations of the elements. The results show that individual baselines must be established for the different formations. This has been done for evaluation of concentrations in mining and mineralized areas. Within each formation the baseline concentrations from the different quadrangles are mostly so similar that a single baseline could be used (table 4). Two exceptions are the expected range of the Catahoula (Ecleto) samples and the selenium expected range of the Oakville (Kenedy) samples. Most of the sampling of anomalous areas is centered around western Karnes County (fig. 1) and requires use of the baseline concentrations from only the Whitsett (Fashing) and Catahoula (Coy City or Falls City) quadrangles. Several of the groups of random samples are not used in this study but could be used in other studies or to evaluate reclamation of present mining areas.

COMPARISON WITH CONCENTRATIONS IN OTHER SOILS

How do the background concentrations of molybdenum, arsenic, selenium, and copper in soils in the South Texas uranium mining area compare with concentrations in soils elsewhere? In particular, are there concentrations either high enough or low enough to suggest potential problems? Caution must be used in comparing with concentrations reported from different labs using different analytical techniques. Ideally, all analytical methods should give similar results, but many interlaboratory comparisons have shown that this is not commonly so. For example, Allcott and Lakin (1974) report analyses on U.S. Geological Survey geochemical exploration reference samples obtained from 85 laboratories. Reported molybdenum concentrations for identical splits of one sample ranged from less than 1 ppm to 110 ppm; reported concentrations for another sample ranged from less than 1 ppm to 320 ppm. Clearly, comparisons must be made with caution. Comparisons here are made only with recently reported concentrations but, even so, some comparisons may be misleading. Analyses of reference samples made during the course of this study are tabulated in Appendix B.

Table 6 summarizes the findings of several recent studies on the concentrations of molybdenum, arsenic, selenium, and copper in soils. With the exception of the analyses reported by Dollahite and others (1972), all concentrations are from natural soils undisturbed by mining.

The only concentrations from South Texas directly comparable to those of this study are from Hossner (1976). The concentrations were measured in soils developed on the Oakville Formation near George West approximately 15 km south of Three Rivers (fig. 1). Copper and arsenic concentrations are very similar, but molybdenum concentrations from Hossner (9 to 25 ppm) are approximately an order of magnitude greater than those from this study. The origin of the difference in molybdenum concentrations is uncertain but is important because the concentrations reported by Hossner are so much higher.

Other published summaries show that most soils of this study have molybdenum, arsenic, and selenium concentrations similar to natural soils elsewhere. Several features are important. Almost all studies report a strong influence of parent bedrock concentrations on soil concentrations. Kubota (1977) gives a median of 1 ppm molybdenum for soils throughout the United States but indicates that there is a regional trend. Soils of the eastern United States have generally low molybdenum

TABLE 6. REPORTED CONCENTRATIONS OF TRACE ELEMENTS IN SOILS*

Location	Mo	Cu	Se	As	Reference
South Texas					
Karnes County**					
Soil	(2.7-8.0)	(1.5)			Dollahite and others, 1972
Grass	(15.5-45)	(2.1-25)			
Near George West, Live Oak County	(9-25)	(4-13)		(1.1-4.9)	Hossner, 1976
United States					
United States	1 (0.08-30)				Kubota, 1977
Missouri	3	11 to 23	0.27 to 0.74	5 to 13	Connor and Shacklette, 1975
Georgia					
high mortality		8.7 (A),***8.8 (B)			Shacklette and others, 1970
low mortality		26 (A), 29 (B)			
Piceance Creek Basin, Colorado	5.3 (1-14)	29 (8.7-122)	0.28 (0.1-1.2)	6.4 (2-21)	Ringrose and others, 1976
Powder River Basin, Montana, Wyoming		15 (A), 17 (B)	0.22 (A), 0.28 (B)		Tidball, 1975;
			0.10 (A), 0.05 (B)	6 (A), 6.6 (B)	Anderson and others, 1975
Others					
Great Britain	1	20	1		Mitchell, 1971
Worldwide?				5 to 6 (0.1-40)	National Academy of Sciences, 1977a
Worldwide				7.2 (0.1-55)	Boyle and Jonasson, 1973

* Mean (range) in ppm

** Uranium mining site

*** A=A horizon; B=B horizon.

concentrations (less than 1 ppm); soils of the western United States have higher concentrations (greater than 2 ppm). The differences are related to bedrock. This observation is substantiated by the results of several studies from parts of the western United States (Table 6). The results of Kubota (1977), Mitchell (1971), and Connor and Shacklette (1975) indicate that a molybdenum concentration of 1 ppm is a reasonable worldwide average. Molybdenum concentrations of some soils of this study, mostly those developed on the Whitsett Formation, have higher concentrations comparable to concentrations reported for soils of the western United States.

Soils of this study differ most markedly from other soils in their copper concentrations. Mean copper concentrations found in this study range from 5.5 to 10.8 ppm or no more than one-half that found in a variety of other soils. An interesting comparison can be made with copper concentrations in soils in Georgia (Shacklette and others, 1970). Two separate areas of different copper concentrations show different cardiovascular mortality rates. The high mortality area has concentrations comparable to those of this study (5 to 10 ppm). The low mortality area has copper concentrations (26 to 29 ppm) several times those of the high mortality area or of the South Texas uranium district. Shacklette and others (1970) found similar differences in several other trace elements and speculated on a relationship of mortality rates to nutritional deficiencies. This does not imply that the South Texas area could have a high cardiovascular mortality rate. However, the overall comparison of copper concentrations indicates that soils of the uranium mining area have distinctively low copper concentrations.

Dollahite and others (1972) report copper and molybdenum concentrations of soil and grass from a pasture in a uranium mining area in Karnes County near the southwestern corner. According to Dollahite, cattle grazing on the pasture had developed signs of "copper deficiency and/or molybdenosis." Copper concentration in soils found by Dollahite are even lower than those found in this study, although copper concentrations in grass are only slightly lower. Molybdenum concentrations in grass are very much higher than those found in this study, although molybdenum concentrations in soil are similar to or slightly greater than those found in soils of the Whitsett Formation (Table 6). Soil pH reported by Dollahite ranges from 5.1 to 5.7. At such low pH, greater relative availability of copper than molybdenum should be expected, but Dollahite's results did not show this. The origin of the differences is uncertain. They may result from differences in analytical techniques; alternatively, the high molybdenum concentrations reported by Dollahite could result from direct contamination of grass by mine wastes.

Copper and molybdenum concentrations and copper/molybdenum ratios in vegetation elsewhere are not widely available; those available are from widely different species of vegetation, and most are reported as concentrations in plant ash. For these reasons, it is not possible to make comparisons of concentrations in vegetation.

From the overall comparison, it can be concluded that most soils in the uranium mining areas have molybdenum, arsenic, and selenium concentrations similar to other natural soils around the United States and worldwide. However, some soils developed on the Whitsett Formation have measurably higher molybdenum concentrations, and all soils have distinctively lower copper concentrations compared to natural soils from a variety of locations.

SECTION 6

RESULTS OF MINING AND MINERALIZED AREA STUDIES

The following section presents results of sampling around mining areas and areas of suspected shallow mineralization. General locations of these areas are shown in figure 1. All analyses are listed in Appendix A, table A-2. Many of the results are also plotted on maps of the individual areas. Correlation coefficients between copper and molybdenum, molybdenum and arsenic, and molybdenum and selenium are listed in table A-4.

To identify anomalously high concentrations, these samples are compared to the expected ranges determined from the random sampling. The particular range used is determined by the formation and quadrangle in which the tested sample lies.

STOELTJE SITE

Mining at the Stoeltje site (figs. 1 and 5) began in 1972 with excavation of overburden. Mining was completed in 1975, and most of the area was reclaimed (overburden piles shaped and covered with topsoil) by 1977. The ore body was in the Whitsett Formation. The Catahoula Formation occurs at the surface and there is no surface mineralization. Thus any anomalously high concentrations at the surface should have resulted only from mining activities.

Samples were collected from five locations upwind and from five locations downwind of the mine area to evaluate wind transport (fig. 5 and table A-2). Also, three locations (4, 6, 7) were sampled near the edge of the southeasternmost spoil pile where the spoil had not been totally reclaimed. A steep wall of overburden there had been severely eroded with an apron of recognizable spoil material extending approximately 100 m from the edge (fig. 6a). One location was sampled on the surface of each of two spoil piles (fig. 6b). At each of these locations the A horizon sample consisted of reclaimed topsoil, whereas the B horizon consisted of overburden. All samples collected at the Stoeltje site were analyzed for molybdenum concentrations only.

Tests for anomalous concentrations can be made by comparison to the expected range of molybdenum concentrations of the Catahoula (Falls City) samples (upper limit=1.33 ppm; table 4). Two samples, one upwind (5B, 2.6 ppm molybdenum) and one downwind (10B, 1.7 ppm) are greater than the expected range. However, both anomalous samples are from the B horizon and because one is upwind and one downwind, it is unlikely that wind transport of material is responsible for their slightly higher concentrations. More likely, they are natural concentrations.

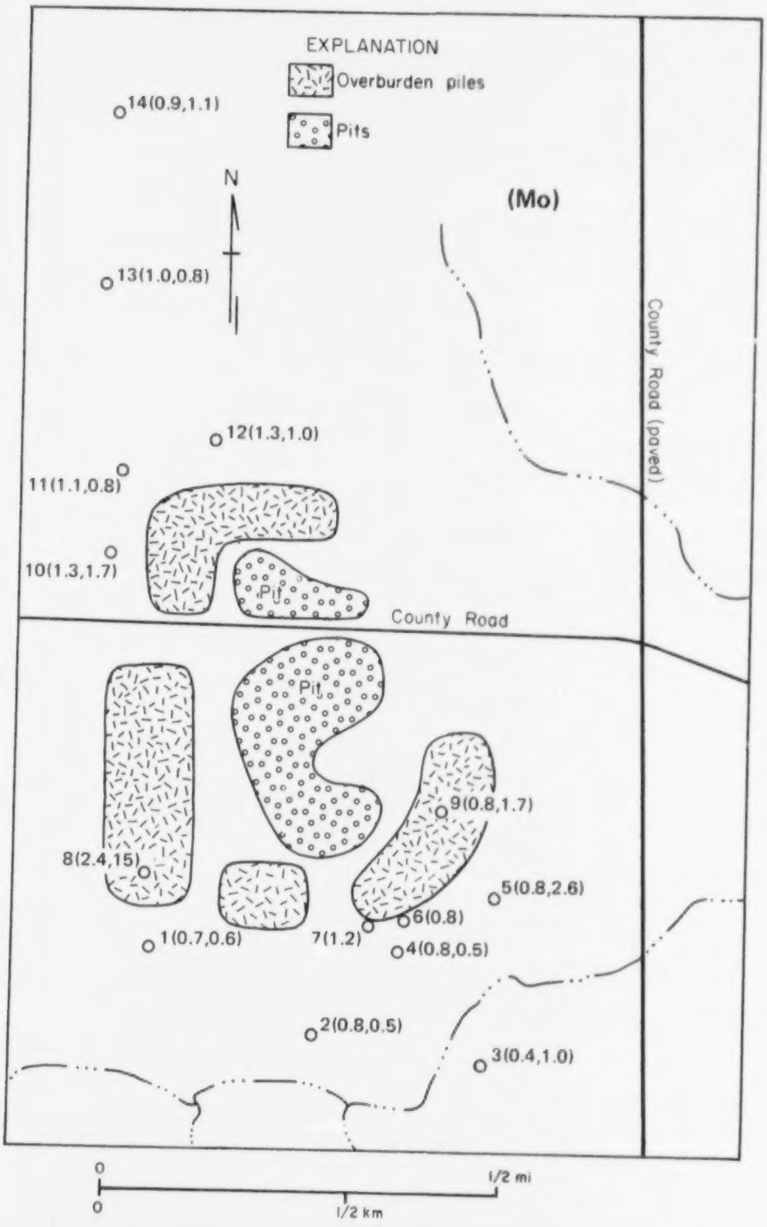
EXPLANATION
Overburden piles
Pits
(Mo)
N
14(0.9,1.1)
13(1.0,0.8)
12(1.3,1.0)
11(1.1,0.8)
10(1.3,1.7)
Pit
County Road
County Road (paved)
Pit
9(0.8,1.7)
8(2.4,15)
5(0.8,2.6)
6(0.8)
7(1.2)
1(0.7,0.6)
4(0.8,0.5)
2(0.8,0.5)
3(0.4,1.0)
0
1/2 mi
0
1/2 km

Figure 5. Index map of the Stoeltje mining area showing sample locations (circles), mine pits, and reclaimed overburden piles. Values in parentheses following sample locations are molybdenum concentrations in ppm in A and B horizon samples, respectively. Where only one value is given, it is from the A horizon.

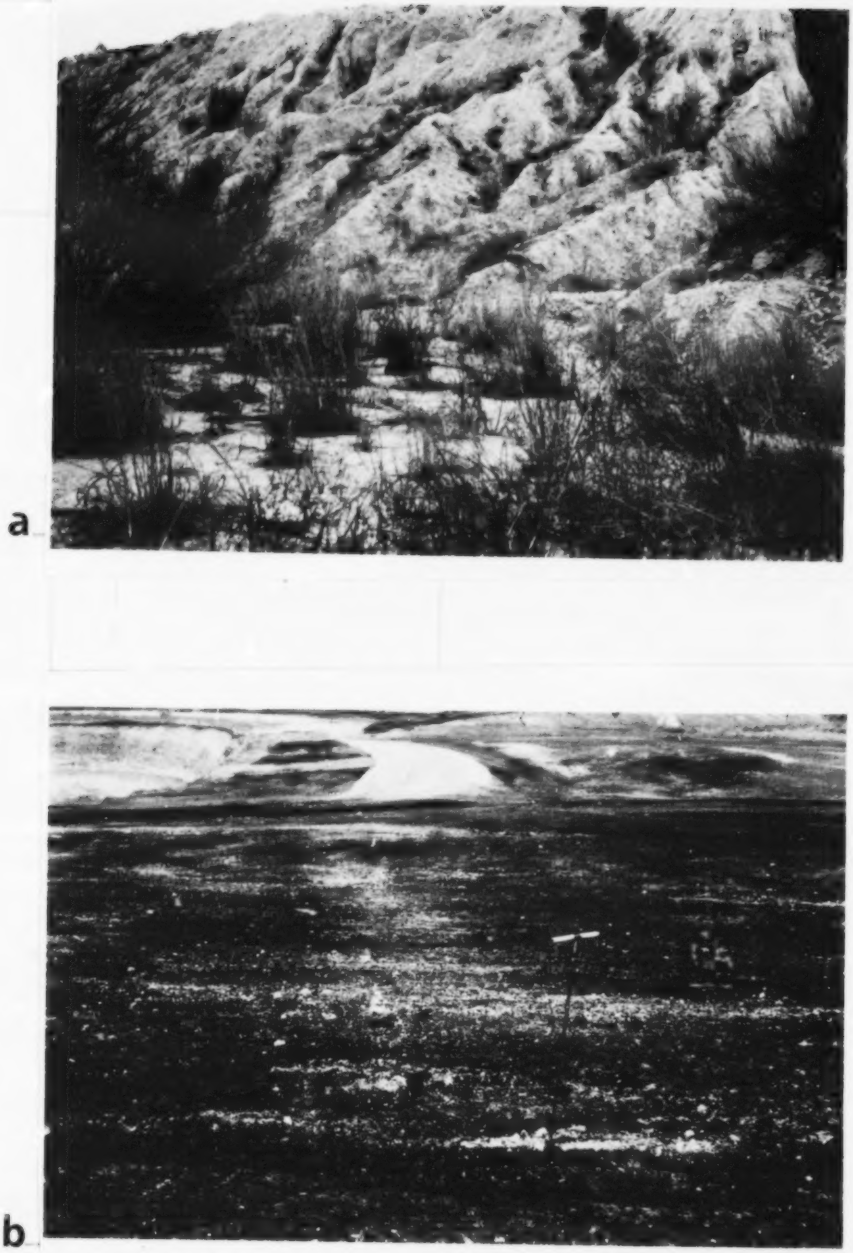

Figure 6. (a) Eroded overburden along south edge of southeasternmost spoil pile at location 6 at Stoeltje site. (b) Reclaimed spoil pile at Stoeltje mine, sample location 8. Dark material is restored topsoil; light material is uncovered overburden. The southern mine pit is on the left.

Molybdenum concentrations of samples from all other upwind (1, 2, 3, 4) and downwind (11, 12, 13, 14) locations are within the expected range. There is a slight pattern of higher molybdenum concentrations downwind, but except for sample 10B, the concentrations are all within the statistically expected range. All concentrations are low and can be explained by natural variation. Clearly, there is no evidence for measurable contamination of the soils from windblown spoil.

Erosion of spoil has produced a wedge-shaped fan of debris extending out from the southern tip of the southeasternmost spoil pile (fig. 6a). The spoil material is light-colored sand and stands out distinctly from the dark, clay-rich soil. Samples of eroded spoil (locations 6 and 7) and one of soil with a 5-cm coating of spoil (4A) all contain low concentrations of molybdenum. Either overburden here was not enriched in molybdenum or any high molybdenum concentrations once present have been leached out. If the latter is true, the molybdenum has not accumulated in any of the sampled locations.

Locations 8 and 9 are on reclaimed spoil piles where overburden is irregularly exposed (fig. 6b). For each the A horizon is reclaimed topsoil (probably Monteola clay) and the B horizon is overburden. Sample 9B (1.7 ppm molybdenum) is slightly anomalous but less so than samples 5B and 10B; however, sample 8B (15 ppm molybdenum) is distinctly anomalous. Sample 8A (2.4 ppm) is also anomalous, but its molybdenum concentration is less than that of sample 5B whose high concentration is considered natural. The concentration of 8A could be natural, or it could result from minor contamination by overburden either by physical mixing or by chemical transport within the soil.

The molybdenum concentration of sample 8B shows that some overburden is enriched in molybdenum; the concentration is high enough to be of concern. However, only two locations were sampled and cannot be considered representative of the entire reclaimed area. The area is presently being sampled more extensively by the mining company.

The analyzed samples indicate that molybdenum was not transported in measurable concentrations by wind or by runoff from one area of spoil. For that reason no additional analyses for arsenic, selenium, or copper were considered necessary.

FELDER SITE

The Felder area (within the Ray Point district) has experienced two generations of mining. Several mines were active in 1967 at what were called the Felder and McLean mines (Eargle and others, 1973). Figure 7 shows these mines and related disturbed areas. Surface mining has recently been reinitiated in the same area (and same mineralized zone) as the older mining. In addition, several in situ leach plants are either operating or under construction along the same ore trend. The present surface mining operation is reclaiming the old unreclaimed overburden piles left from earlier mining. Nevertheless, the area was left unreclaimed with abandoned, unrevegetated spoil piles susceptible to erosion from 1967 to 1977. Mineralization is in sands of the Oakville Sandstone, and surface mineralization has been reported in sands which crop out at locations 3, 4, and 5 (W. E. Galloway, personal communication) (figure 7). Identification of anomalous concentrations is made by comparison with the upper limit of the Oakville (Ray Point) samples (1.89 ppm Mo).

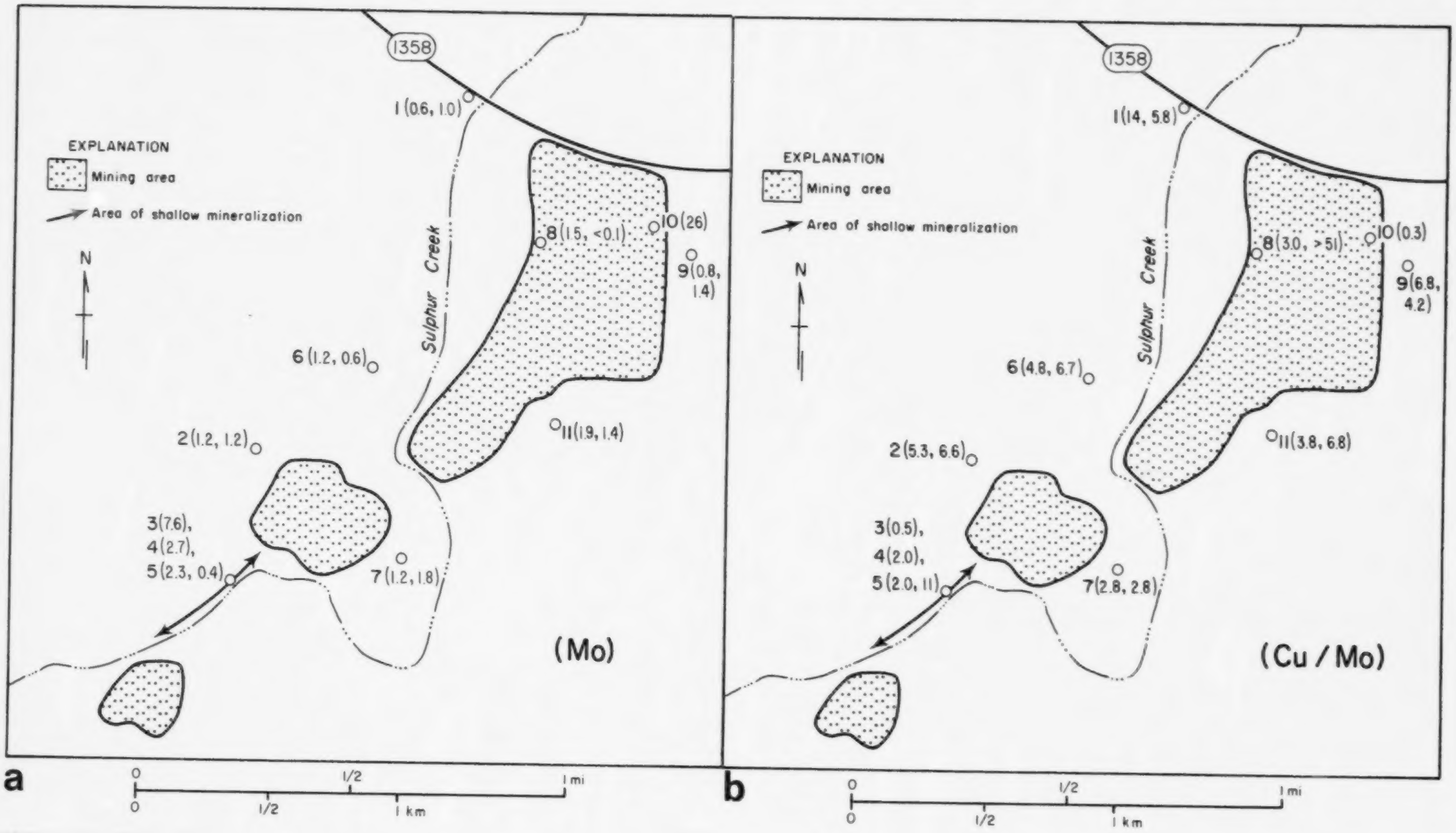
EXPLANATION
Mining area
Area of shallow mineralization
N
1358
Sulphur Creek
1 (0.6, 1.0)
2 (1.2, 1.2)
3 (7.6),
4 (2.7),
5 (2.3, 0.4)
6 (1.2, 0.6)
7 (1.2, 1.8)
8 (1.5, <0.1)
9 (0.8, 1.4)
10 (26)
11 (1.9, 1.4)
(Mo)
a
0
1/2
1 mi
0
1/2
1 km
EXPLANATION
Mining area
Area of shallow mineralization
N
1358
Sulphur Creek
1 (14, 5.8)
2 (5.3, 6.6)
3 (0.5),
4 (2.0),
5 (2.0, 11)
6 (4.8, 6.7)
7 (2.8, 2.8)
8 (3.0, >51)
9 (6.8, 4.2)
10 (0.3)
11 (3.8, 6.8)
(Cu / Mo)
b
0
1/2
1 mi
0
1/2
1 km

Figure 7. Index map of the Felder site showing sample locations (circles) and extent of older mining area, which includes mine pits, spoil piles, and related disturbed areas. (a) Molybdenum concentrations in ppm are in parentheses following sample locations. (b) Copper/molybdenum ratios in parentheses following sample locations. For each first value is for A horizon, second value is B horizon. Samples 3 and 4 are from sandstone outcrop.

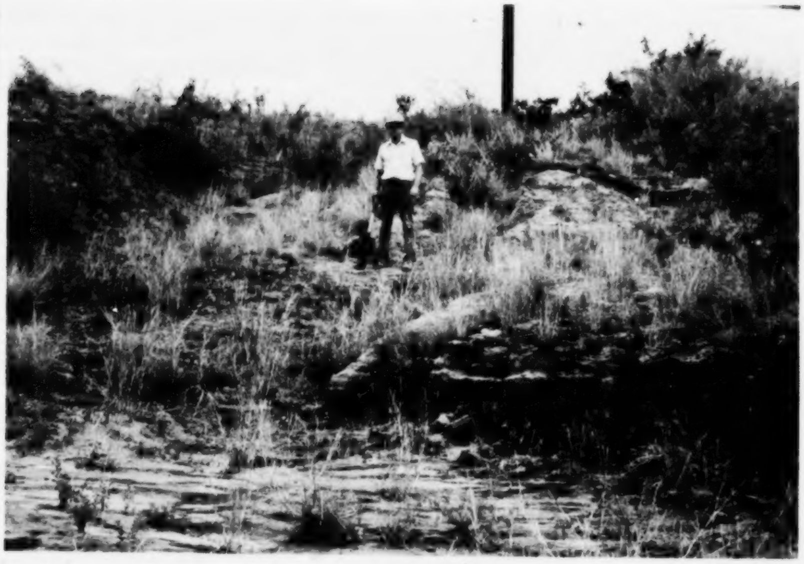

Figure 8. Outcrop of basal sand of Oakville Sandstone near locations 3, 4, and 5, Felder site.

Oakville ore in this area is commonly considered molybdenum rich; reported molybdenum concentrations of ore and overburden are as high as 275 ppm in ore and 32 ppm in existing spoil (Exxon, 1976). These concentrations were obtained by an unspecified anion extraction and are not comparable to analyses of this study. A sample of low-grade ore (location 10) collected for this study contains 26 ppm molybdenum.

A and B horizon samples were collected from three locations upwind (7, 9, 11) and three locations downwind (1, 2, 6) from the former mining operations (fig. 7, table A-2). All these samples have molybdenum concentrations below or at most equal to the upper limit of the expected range of 1.89 ppm. Sample 11A with 1.9 ppm molybdenum, the highest concentration found of these samples, was collected upwind of the mining site.

Copper concentrations of the samples range from 3.4 to 9.5 ppm. All are within the expected range (upper limit of 13.1 ppm) and, in fact, soils of the mining area have noticeably lower copper concentrations than in the Oakville (Ray Point) samples. Copper/molybdenum ratios range from 2.8 to 14. The lowest ratios result from low copper concentrations rather than from high molybdenum concentrations.

Two samples of Oakville Sandstone from outcrop (fig. 8) have higher molybdenum concentrations (3A, 7.6 ppm; 4A, 2.7 ppm). Both concentrations are greater than the upper limit for soils and indicate that molybdenum is concentrated in the mineralized sandstone, but the concentrations are not exceptionally high. Both samples are from surface exposures and could have experienced some leaching of molybdenum. If so, the original molybdenum concentrations could have been greater than the measured concentrations. Copper concentrations in the outcrop samples are as low as any determined in soils.

Soil developed on the sandstone outcrop has been disturbed by bulldozing for nearby construction of a mining road so concentrations in the soils have to be evaluated cautiously. Molybdenum concentration in the A horizon (5A, 2.3 ppm) is only slightly greater than the upper limit; molybdenum in the B horizon sample is quite low (0.5 ppm). Copper concentrations are also low.

It was an intent of this project to sample stream sediment within Sulphur Creek (fig. 7). However, at the time of this sampling Sulphur Creek was flowing due to heavy rains (it is dry most of the year) and could not be sampled. The older spoil had been deposited directly adjacent to the creek both at the Felder site and upstream with no protective berm. Erosion and runoff have occurred from the spoil piles and from areas of mineralized outcrop. Thus it is very possible that there are high molybdenum concentrations in sediments in Sulphur Creek. A single sediment sample, taken for a geochemical exploration program from Sulphur Creek approximately 4 km downstream from the mining area, had molybdenum, selenium, and arsenic concentrations of 2 ppm, 1.7 ppm, and 10.5 ppm, respectively (Nichols and others, 1977). The molybdenum concentration may be slightly anomalous. The selenium concentration is distinctly anomalous. Arsenic concentrations have not been determined in background samples in the area, but compared to Catahoula (Comanche Hills) concentrations, the arsenic concentration in Sulphur Creek is not anomalous. Stream sediments in Sulphur Creek should be sampled and analyzed more thoroughly to document actual concentrations and their sources.

WEDDINGTON AREA AND MEXICAN HOLLOW

The Weddington area is one of the more critical areas for evaluation of the effects of mining. Most complaints of molybdenosis have centered around Mexican Hollow, the major drainage from this mining area.

The Weddington area is named for several of the early mine pits, which in turn were named for the landowner from whom mining rights were acquired. However, this area includes a nearly continuous trend of mineralization and mines with a variety of names which extend to the north of figures 9 to 12. Mining began in 1963 and continues today. Reclamation was not practiced until 1975, and many mine areas remain unreclaimed. However, several older mining areas were reclaimed when adjacent areas were mined recently.

Uranium ore occurs in sands of the Whitsett Formation at depths of approximately 30 m. The surface is dominantly Catahoula Formation outcrop. Thus, shallow mineralization should not be a source for high molybdenum (or other element) concentrations except for a few exceptions discussed below. Wind transport of material exposed in unreclaimed spoil piles, and erosion and water transport of overburden from spoil piles are possible sources of contamination. Also, until about 1973, water discharged into mining pits from the permeable host sands was pumped from the pits into adjacent drainages. Present regulations do not allow open discharge of mine water, so contamination by this method, if it ever occurred, should not be occurring today. Samples collected in the Weddington area come from the outcrop of Catahoula and Whitsett Formations (figs. 9 to 12). Thus, measured concentrations

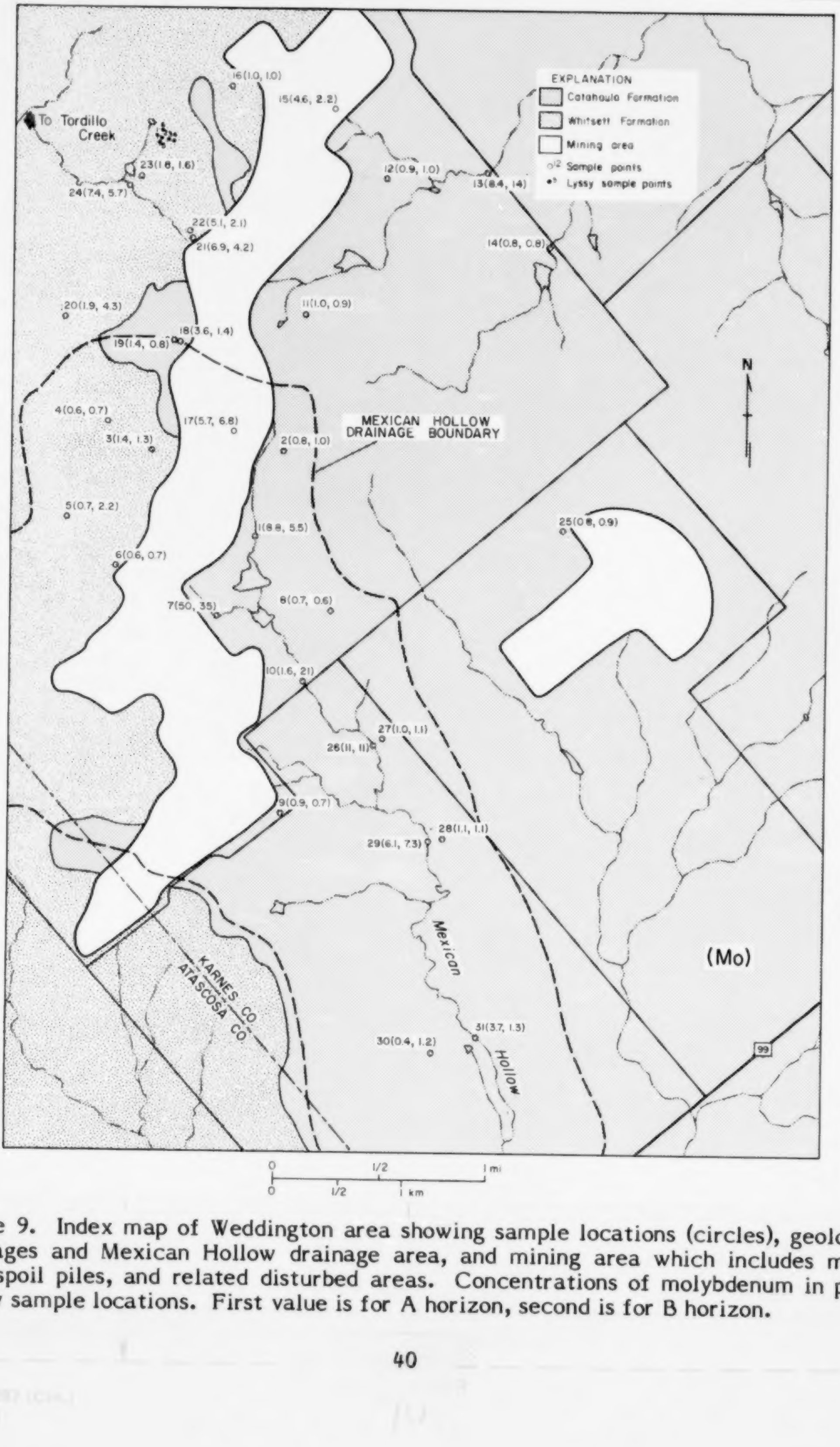
EXPLANATION
Catahoula Formation
Whitsett Formation
Mining area
○12 Sample points
•5 Lyssy sample points
To Tordillo Creek
16(1.0, 1.0)
15(4.6, 2.2)
23(1.6, 1.6)
24(7.4, 5.7)
12(0.9, 1.0)
13(8.4, 14)
22(5.1, 2.1)
21(6.9, 4.2)
14(0.8, 0.8)
20(1.9, 4.3)
11(1.0, 0.9)
18(3.6, 1.4)
19(1.4, 0.8)
N
4(0.6, 0.7)
17(5.7, 6.8)
MEXICAN HOLLOW DRAINAGE BOUNDARY
3(1.4, 1.3)
2(0.8, 1.0)
5(0.7, 2.2)
1(8.8, 5.5)
25(0.8, 0.9)
6(0.6, 0.7)
7(50, 35)
8(0.7, 0.6)
10(1.6, 21)
27(1.0, 1.1)
26(11, 11)
9(0.9, 0.7)
28(1.1, 1.1)
29(6.1, 7.3)
Mexican
(Mo)
KARNES CO
ATASCOSA CO
30(0.4, 1.2)
31(3.7, 1.3)
Hollow
99
0
1/2
1 mi
0
1/2
1 km

Figure 9. Index map of Weddington area showing sample locations (circles), geology, drainages and Mexican Hollow drainage area, and mining area which includes mine pits, spoil piles, and related disturbed areas. Concentrations of molybdenum in ppm follow sample locations. First value is for A horizon, second is for B horizon.

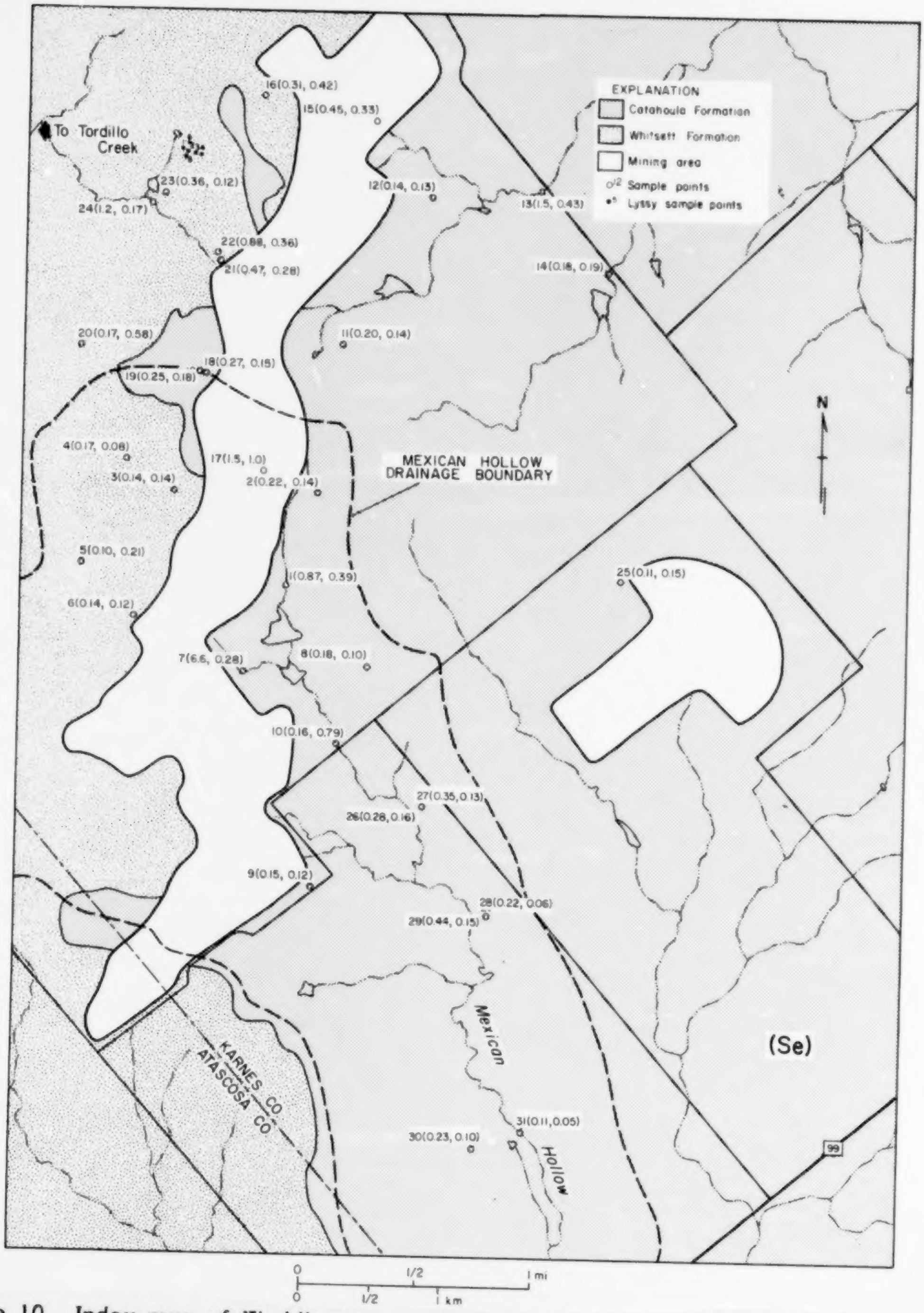
EXPLANATION
Catahoula Formation
Whitsett Formation
Mining area
Sample points
Lyssy sample points
To Tordillo Creek
16(0.31, 0.42)
15(0.45, 0.33)
23(0.36, 0.12)
24(1.2, 0.17)
12(0.14, 0.13)
13(1.5, 0.43)
22(0.88, 0.36)
21(0.47, 0.28)
14(0.18, 0.19)
20(0.17, 0.58)
11(0.20, 0.14)
18(0.27, 0.15)
19(0.25, 0.18)
N
4(0.17, 0.08)
17(1.5, 1.0)
3(0.14, 0.14)
2(0.22, 0.14)
MEXICAN HOLLOW DRAINAGE BOUNDARY
5(0.10, 0.21)
1(0.87, 0.39)
25(0.11, 0.15)
6(0.14, 0.12)
7(6.6, 0.28)
8(0.18, 0.10)
10(0.16, 0.79)
27(0.35, 0.13)
26(0.28, 0.16)
9(0.15, 0.12)
28(0.22, 0.06)
29(0.44, 0.15)
Mexican
Hollow
(Se)
KARNES CO
ATASCOSA CO
31(0.11, 0.05)
30(0.23, 0.10)
99
0
1/2
1 mi
0
1/2
1 km

Figure 10. Index map of Weddington area showing sample locations (circles), geology (from Dickinson, 1975), drainages and Mexican Hollow drainage area, and mining area which includes mine pits, spoil piles, and related disturbed areas. Concentrations of selenium in ppm follow sample locations. First value is for A horizon, second is for B horizon.

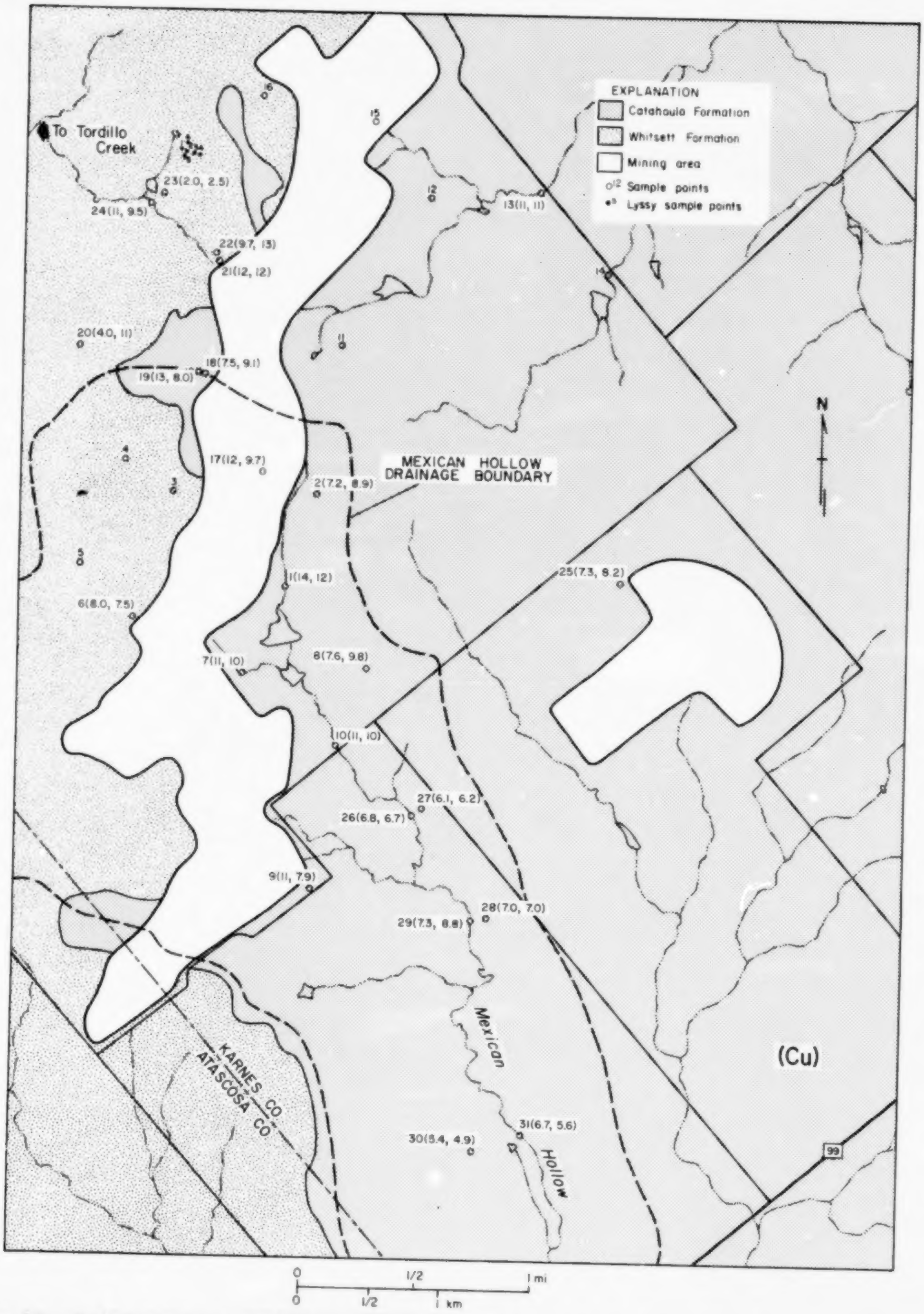
EXPLANATION
Catahoula Formation
Whitsett Formation
Mining area
Sample points
Lyssy sample points
To Tordillo Creek
16
15
12
13(11, 11)
14
23(2.0, 2.5)
24(11, 9.5)
22(9.7, 13)
21(12, 12)
20(4.0, 11)
11
18(7.5, 9.1)
19(13, 8.0)
4
3
17(12, 9.7)
2(7.2, 8.9)
MEXICAN HOLLOW DRAINAGE BOUNDARY
N
5
1(14, 12)
25(7.3, 8.2)
6(8.0, 7.5)
7(11, 10)
8(7.6, 9.8)
10(11, 10)
27(6.1, 6.2)
26(6.8, 6.7)
9(11, 7.9)
28(7.0, 7.0)
29(7.3, 8.8)
Mexican Hollow
KARNES CO
ATASCOSA CO
(Cu)
31(6.7, 5.6)
30(5.4, 4.9)
99
0
1/2
1 mi
0
1/2
1 km

Figure 11. Index map of Weddington area showing sample locations (circles), geology (from Dickinson, 1975), drainages and Mexican Hollow drainage area, and mining area which includes mine pits, spoil piles, and related disturbed areas. Concentrations of copper in ppm follow sample locations. First value is for A horizon, second is for B horizon.

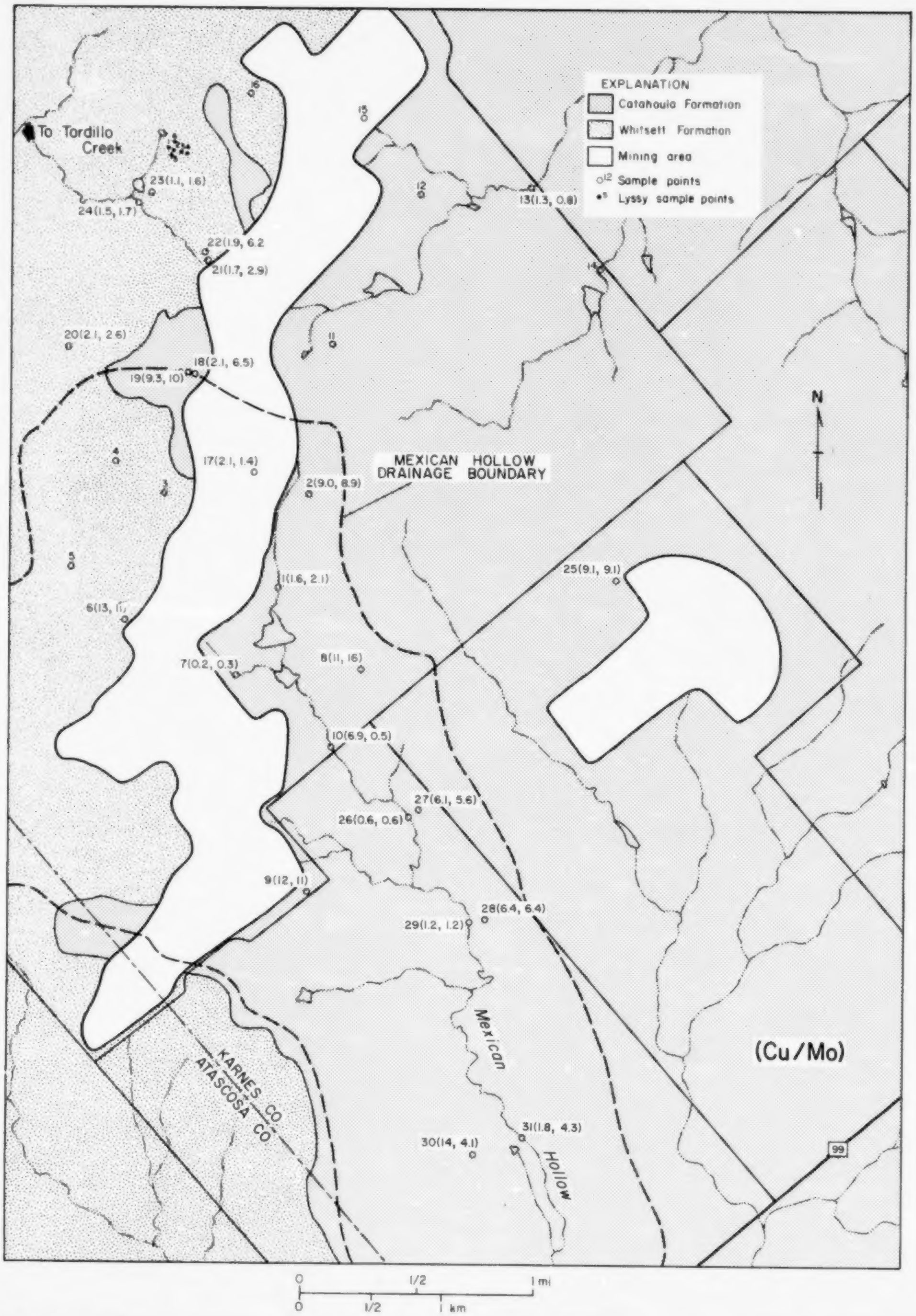
EXPLANATION
Catahoula Formation
Whitsett Formation
Mining area
Sample points
Lyssy sample points
To Tordillo Creek
MEXICAN HOLLOW DRAINAGE BOUNDARY
N
KARNES CO.
ATASCOSA CO.
Mexican Hollow
99
(Cu/Mo)
23(1.1, 1.6)
24(1.5, 1.7)
22(1.9, 6.2
21(1.7, 2.9)
20(2.1, 2.6)
18(2.1, 6.5)
19(9.3, 10)
17(2.1, 1.4)
2(9.0, 8.9)
1(1.6, 2.1)
6(13, 11)
7(0.2, 0.3)
8(11, 16)
10(6.9, 0.5)
27(6.1, 5.6)
26(0.6, 0.6)
9(12, 11)
28(6.4, 6.4)
29(1.2, 1.2)
25(9.1, 9.1)
13(1.3, 0.8)
30(14, 4.1)
31(1.8, 4.3)
16
15
12
14
11
4
3
5
0
1/2
1 mi
0
1/2
1 km

Figure 12. Index map of Weddington area showing sample locations (circles), geology (from Dickinson, 1975), drainages and Mexican Hollow drainage area, and mining area which includes mine pits, spoil piles, and related disturbed areas. Copper/molybdenum ratios follow sample locations. First value is for A horizon, second is for B horizon.

necessarily are evaluated against different background concentrations. Soils collected from areas of Catahoula Formation are compared with Catahoula (Coy City) samples (table 4). Soils from the Whitsett Formation are compared with Whitsett (Fashing) samples (table 4).

Wind Transport

Samples were collected upwind and downwind of the main line of mine pits and spoil (figs. 9 to 12). Both A and B horizon samples were collected from all Weddington area locations. Sample locations upwind include numbers 2, 8, 9, 11, and 12. Sample locations 27, 28, and 30 were used for comparison with locations within the Mexican Hollow drainage but can also be used as upwind samples. All of these samples are from areas underlain by the Catahoula Formation. Molybdenum concentrations of these samples range from 0.6 to 1.2 ppm (table A-2 and figs. 9 to 12) and are very similar to the background concentrations from Catahoula (Coy City) samples. Selenium concentrations of the upwind samples vary from 0.10 to 0.22 ppm, and are similar to selenium concentrations of Catahoula (Coy City) samples. Thus, the background samples from the barbell sampling scheme could have been used in place of these upwind samples to determine upwind baseline concentrations for the Weddington area.

Samples collected downwind from the mining area include locations 3, 4, 5, 6, 16, and 20. Most of these samples are from areas of Whitsett outcrop, and all except location 20 are from the Fashing Clay Member. Molybdenum concentrations in downwind samples other than from location 20 range from 0.6 to 2.2 ppm. None of these concentrations are anomalous compared to the Whitsett (Fashing) upper limit of 6.05 ppm. In fact, molybdenum concentrations of all but samples 5B (2.2 ppm) are within the upper limit of 1.6 ppm for Catahoula (Coy City) samples. As discussed above, the clayey parts of the Whitsett Formation away from the mineralized sands have trace element concentrations distinctly lower than concentrations in the mineralized sands. Thus, evaluation of background by comparison with Catahoula (Coy City) samples might be more appropriate. This is an example where failure to recognize subenvironments within individual formations could be misleading. In any event, neither comparison indicates measurable wind transport of molybdenum.

Location 20, on the other hand, has higher molybdenum concentrations (20A, 1.9 ppm; 20B, 4.3 ppm). Soil at location 20 is relatively sandy (although mapped as Monteola Clay) and sandstone rock fragments are abundant. Thus it is similar in texture and molybdenum concentrations to Whitsett (Fashing) samples; evaluation by comparison with Whitsett (Fashing) samples is appropriate. The higher molybdenum concentrations at location 20 are probably natural, and are additional indications of the minor mineralization found associated with Whitsett sands.

Selenium concentrations of downwind samples largely parallel molybdenum concentrations. All are less than the Whitsett (Fashing) upper limit (1.1 ppm), and all but two (16B, 0.42 ppm; 20B, 0.58 ppm) are less than the Catahoula (Coy City) upper limit (0.32 ppm). As discussed for the molybdenum concentrations, sample 20B should be evaluated with the Whitsett (Fashing) samples. Location 16 is largely surrounded by mines or spoil piles and may have received some contamination. It does not however, have an anomalous molybdenum concentration. Together the pattern of molybdenum and selenium concentrations show that wind transport is not a significant source of contamination.

Copper concentrations were not determined for all Weddington area samples. Concentrations of those determined range from 4.0 to 11 ppm with all but one greater than 7 ppm. Copper/molybdenum ratios in all but the A and B horizon samples from location 20 (20A, 2.1; 20B, 2.6) are greater than 8.9. Sample 20A has a low copper concentration (4.0 ppm) and subsequently a low copper/molybdenum ratio (2.1). Sample 20B has a higher copper concentration (11 ppm), higher in fact than the upper limit for Whitsett (Fashing) samples, but its relatively high molybdenum concentration gives it a low copper/molybdenum ratio (2.6). Copper concentrations and copper/molybdenum ratios of samples along Mexican Hollow are discussed below.

Location 17 is within a reclaimed area. Sample 17A consists of reclaimed top soil whereas sample 17B is reworked overburden. Both samples have relatively high molybdenum and selenium concentrations (17A, 5.7 ppm and 1.5 ppm; 17B, 6.8 and 1.0 ppm). If the reclaimed soil is locally derived, the most plausible source, then its high molybdenum and selenium concentrations must be due to some interaction with the overburden. Physical mixing of the texturally distinct soil and overburden has occurred in this and other reclaimed areas, but not in sample 17A. Possibly the trace elements were redistributed by upward moving soil water. Copper concentrations of both samples are within expected limits and coupled with the high molybdenum concentrations, give very low copper/molybdenum ratios (2.1 and 1.4).

Runoff from Spoil Piles

At several locations visited in this study, the protective berm designed to catch runoff from spoil piles has broken down or filled up, allowing water and solid material to escape from the spoil pile (fig. 13). This has occurred at sample locations 18 and 19, 21 and 22, along the overburden piles near sample 12 and at the head of the Mexican Hollow drainage. At all but locations 18 and 19, the runoff enters almost directly into local drainages. However, it was reported from several sources that pit waters were also pumped into these drainages. Thus concentrations found in the drainages could result from both natural sources and from different kinds of runoff from mining areas.

Location 18 is approximately 20 m from an unreclaimed spoil pile; location 19 is 50 m farther from the spoil pile. Both locations are within the Catahoula Formation, so natural soil at each is derived from the Catahoula Formation. At location 18, eroded overburden approximately 25 cm thick covers the natural soil and was sampled as the A horizon (fig. 14). The fan of spoil material extended only a short distance farther and does not reach location 19. Of the four samples only the eroded overburden sample (18A, 3.6 ppm) has a molybdenum concentration greater than the expected range.

The setting of sample locations 21 and 22 is very similar to that of locations 18 and 19. Locations 21 and 22 are in Whitsett outcrop adjacent to a spoil pile where erosion has built a fan of material out from the pile (fig. 13). At location 21 the A horizon sample is from reworked overburden 40 cm thick. The B horizon sample from location 21 and both A and B horizon samples from location 22 are normal soils. Only the molybdenum concentration of sample 21A (6.9 ppm) is greater than the Whitsett (Fashing) upper limit. None of the selenium concentrations are greater than the upper limit. Nevertheless, at each location molybdenum and selenium concentrations of the A horizon samples are greater than concentrations in the B horizon samples. This finding suggests that the soils could have been enriched in both molybdenum and

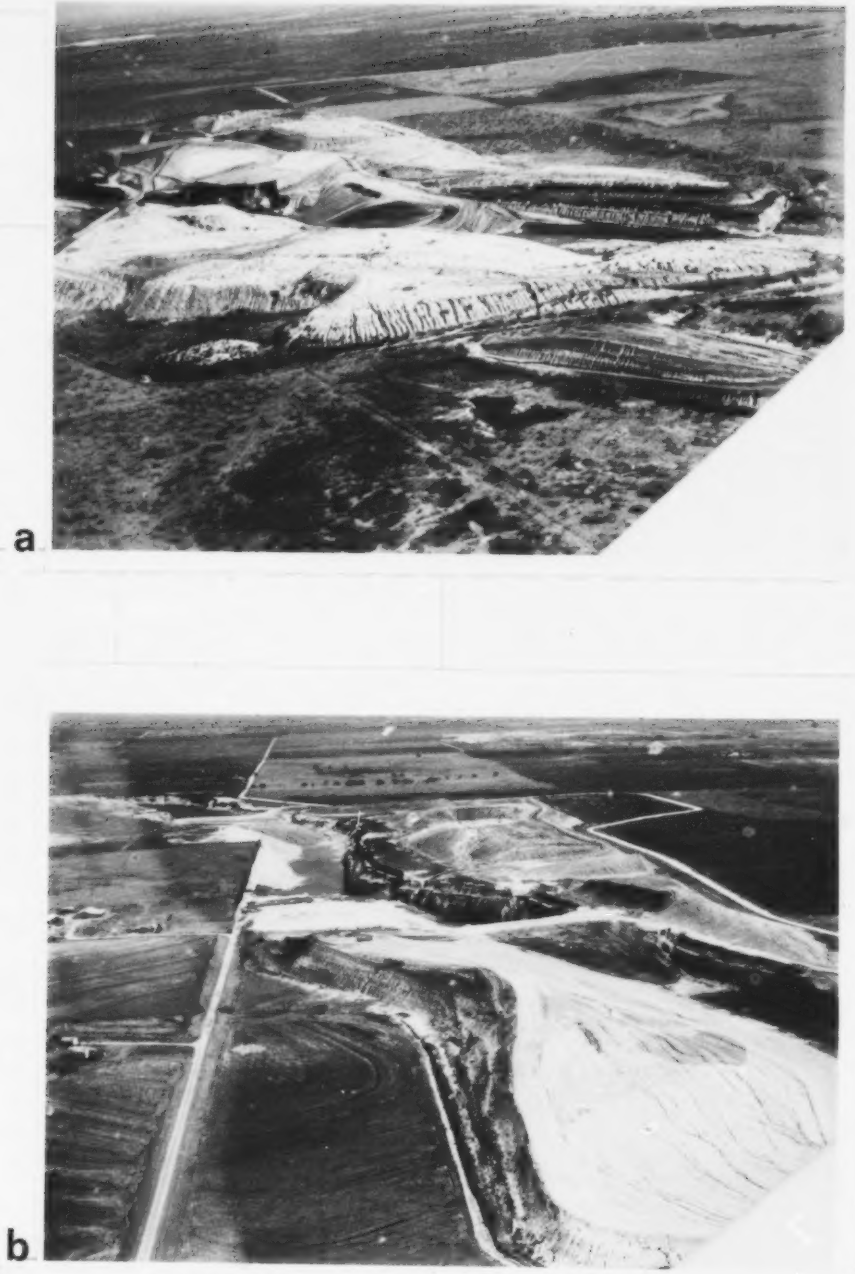

Figure 13. (a) Aerial view of Weddington area showing abandoned mine pits and unreclaimed spoil piles. Sample locations 21 and 22 are at left edge of photo near base of eroded spoil pile. Locations 12 and 13 are at top edge of photo in front of county road. (b) Aerial view of Weddington area showing mine pits and reclaimed and unreclaimed spoil piles. Sample location 9 is near bend in road at upper right. Mexican Hollow is in background.

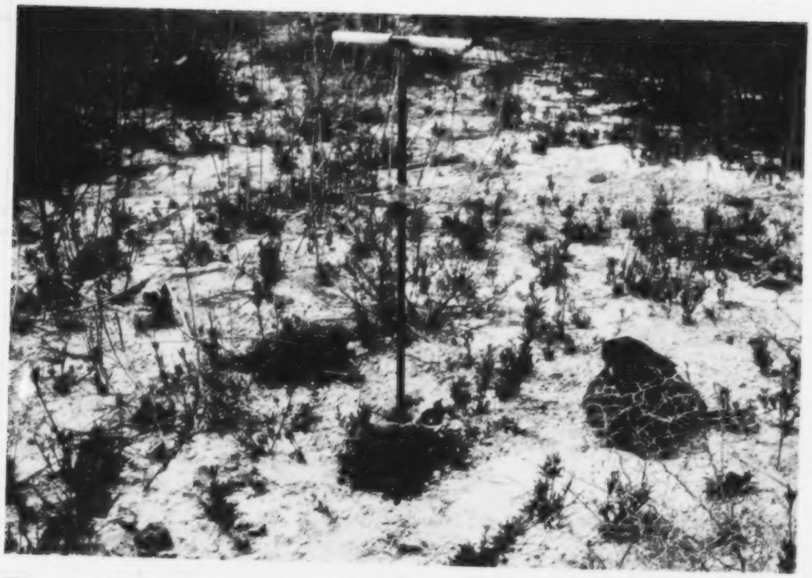

Figure 14. Sample location 18. Light-colored material is overburden eroded from spoil pile behind photographer. Dark material piled in front of sample hole is natural soil from beneath eroded overburden.

selenium from the overburden. However, the concentrations in the soils are not greater than expected concentrations even if they have been altered by runoff.

Samples location 23 and 24 are respectively adjacent to and within a small drainage leading from locations 21 and 22. Molybdenum and selenium concentrations of A and B horizon samples from location 23 are less than the upper limit and, in fact, relatively low in comparison to concentrations in both Whitsett (Fashing) samples and nearby Lyssy area samples. Molybdenum and selenium concentrations in the A horizon sample from location 24 (7.4 ppm molybdenum; 1.2 ppm selenium) are greater than the expected range. Molybdenum concentration in the B horizon is relatively high but less than the upper limit. Selenium concentration in the B horizon is low and well within the upper limit.

The overall pattern of concentrations of samples from location 21 through 24 indicates some contribution of molybdenum and selenium from runoff from the eroding spoil pile. However, nearby, Lyssy area samples also have relatively high molybdenum concentrations and are considered to be natural (discussed below). Although runoff from the Lyssy area enters another drainage, if the concentrations in the Lyssy samples are representative of concentrations over a greater area, natural runoff could also contribute to high molybdenum and selenium concentrations at location 24 and in the drainage from which it was taken.

Sample locations 13 and 14 are on two drainages which intersect areas with and without mining respectively, but are otherwise similar (figs. 9 to 12). A and B horizon samples at location 14 have normal molybdenum and selenium concentrations but at location 13 the concentrations are all greater than upper limits. The high concentrations at location 13 result either from runoff from naturally high concentrations in the original drainage area or from runoff from spoil piles. Molybdenum and selenium concentrations at sample locations 11 and 12 are normal, so most of the drainage area for location 13 cannot be contributing the high concentrations. However, part of the drainage extending to the northwest (in the direction of location 15 on figs. 9 to 12) intersected an area of high surface radioactivity (fig. 3). This area has since been mined but could have contributed to the high concentrations at location 13.

To test the source of molybdenum and selenium at location 13 a small part of the drainage way, cut off and surrounded by mining, was sampled at location 15. Molybdenum and selenium concentrations at this location are moderately high but considerably lower than those at location 13. Location 15 is receiving runoff from spoil piles at present. Without information on concentrations in the drainages before mining it is difficult to identify with certainty the source of the high concentrations in drainage 13. Sampling of runoff from spoil piles along drainage 13 could determine if molybdenum and selenium are being contributed at present.

Mexican Hollow

Much of the concern over molybdenosis and most reported cases center around Mexican Hollow (figs. 9 to 12). Results of this study prove conclusively that there are high concentrations of molybdenum in soils in the channel of Mexican Hollow and that the high concentrations result from runoff from the mines. Whether or not these concentrations have caused or contributed to problems of molybdenosis is a biological question outside the scope of this report. Figures 9 to 12 show the Mexican Hollow drainage area; Mexican Hollow is a broad, low swale without a sharply defined channel. Most of the area including the "channel" is improved pasture (figs. 15 and 16). Ten locations (2, 3, 4, 5, 6, 8, 9, 27, 28, and 30) were sampled within the drainage area to assess natural contributions of molybdenum (figs. 9 to 12). The 20 samples have uniformly low molybdenum concentrations (table A-2). Aeroradioactivity maps of the drainage area (fig. 3) Eargle and Moxham, 1961; Eargle and others, 1961; Moxham and Eargle, 1961) show two areas of slightly higher radioactivity to the west and east. Soil samples taken in these areas all have low concentrations. The eastern of the two areas is mostly within the drainage represented by location 14. Molybdenum and selenium concentrations in samples from location 14 are low. A single sample from Catahoula outcrop (31D) also has a low molybdenum concentration. Thus, no known natural sources for high molybdenum concentrations exist in the Mexican Hollow drainage.

Six locations (1, 7, 10, 26, 29, and 31) were sampled within the actual channel (figs. 9 to 12 and 17). Mexican Hollow is dry most of the year and contains water (other than ponded water) only after rains. Molybdenum (and selenium in some samples) are uniformly high. More important, the molybdenum distribution shows a distinct pattern (fig. 18a). The highest concentrations are from location 7 nearest to the spoil piles. Concentrations decrease downstream; location 31, the farthest downstream has concentrations only slightly above background. Selenium concentrations follow a similar pattern but drop to background levels much more quickly (fig. 18b).

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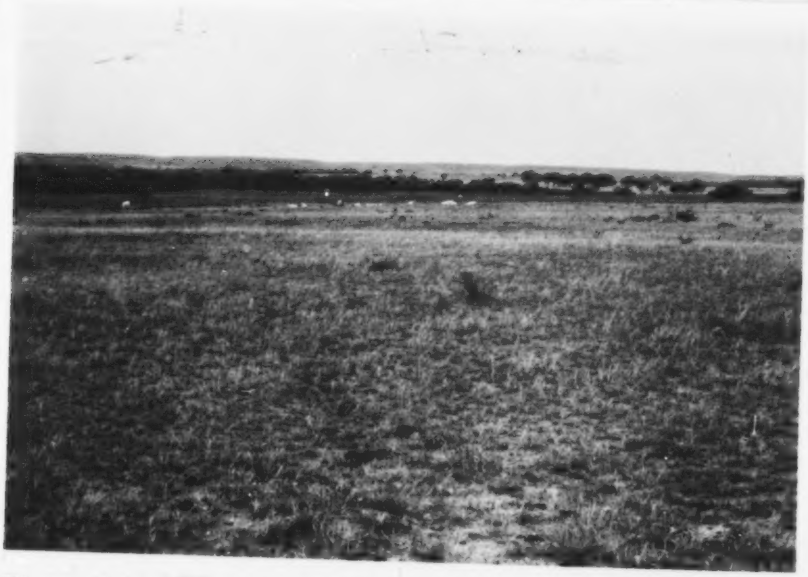

Figure 15. Pasture adjacent to Mexican Hollow with overburden piles on horizon. Photographer looking west from near location 28. Note thin grass cover.

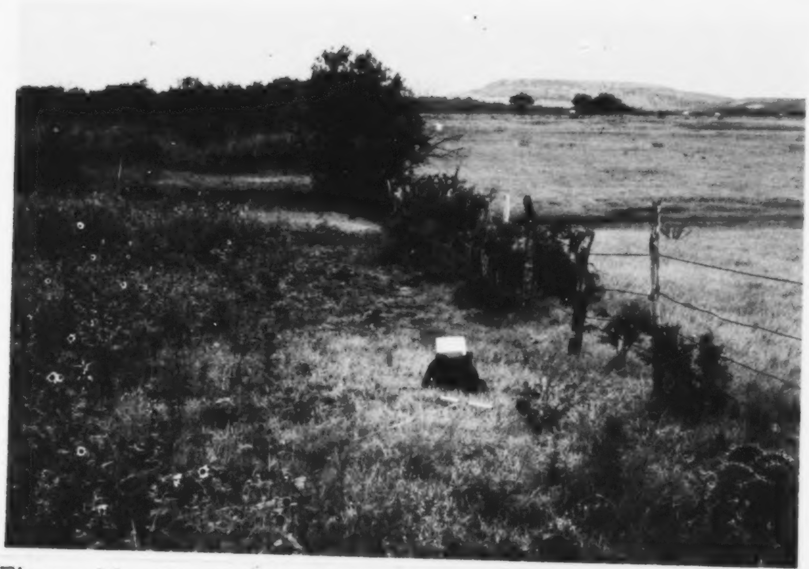

Figure 16. Mexican Hollow drainage runs from right to left across center of photograph; overburden pile in background on right. Photographer looking west from near location 27.

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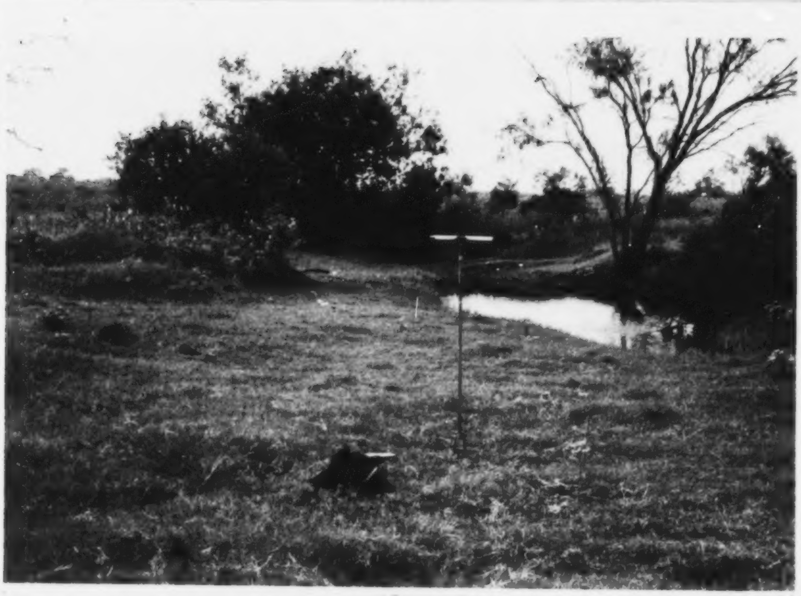

Figure 17. Sample location 26 within channel of Mexican Hollow which is dry except for ponded water, looking downstream. Note thick grass cover.

Copper concentrations were determined in most of the channel and drainage area samples. Concentrations range from 4.9 to 11 ppm in the drainage area and from 5.6 to 14 ppm in the channel. Copper/molybdenum ratios are about 10 in the upper part of the drainage area (near the actual mining site). In the lower part of the drainage area the ratios are significantly lower. Copper/molybdenum ratios in samples from locations 27, 28, and 30 are about 6 with one exception. The lower ratios in this part of the drainage area result from low copper concentrations rather than high molybdenum concentrations. Copper/molybdenum ratios in the channel are very low largely because of the high molybdenum concentrations.

Uptake by plants of copper and molybdenum in the soils is dependent upon the availability of the elements. Molybdenum ought to be proportionately more available than copper in the high pH and poorly drained soils of the area. This supposition was tested by analyzing Bermudagrass from locations 26 through 31. At all but locations 27 and 31, the grass concentrated molybdenum relative to copper. Grass samples 27C and 31C have exceptionally high copper concentrations (27C, 46 ppm; 31C, 80 ppm), confirmed by replicate analyses. Nevertheless, the concentrations are difficult to explain in comparison with other results. Because they are important to understanding potential problems of molybdenosis, more thorough investigation is needed.

Molybdenum concentrations or copper/molybdenum ratios (table A-2) in grass except for the two anomalous samples are at levels at which molybdenosis is likely to occur (Alloway, 1973). This is true not only for grass samples 26C (23 ppm Mo; Cu/Mo=0.36) and 29C (18; 0.48) collected within the channel, but also for samples 28C (2.9; 1.7) and 30C (1.8; 2.6) from outside the channel. Thus, problems of molybdenosis could occur regardless of the effects of mine drainage. However, contamination of

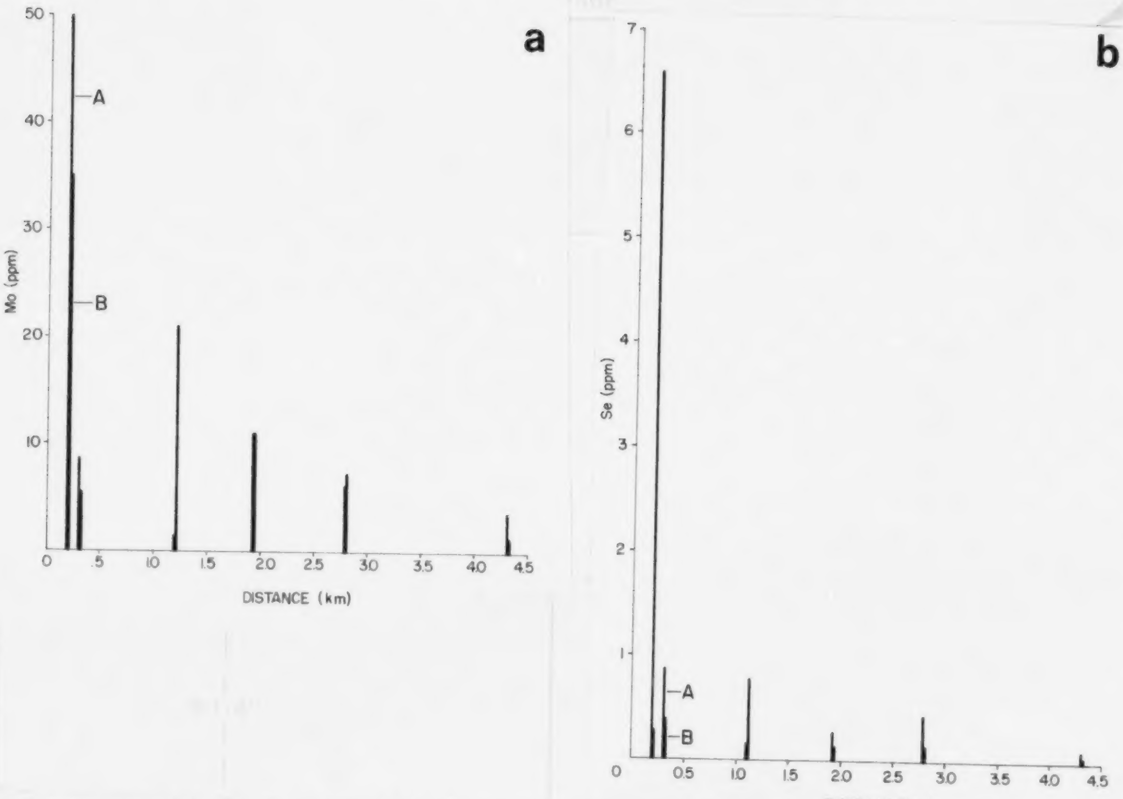

Figure 18. (a) Graph of molybdenum concentration plotted against distance downstream from abandoned spoil piles. (b) Graph of selenium concentration plotted against distance downstream from abandoned spoil piles. A and B denote A and B soil horizons, respectively.

the stream beds with molybdenum from mine runoff may have aggravated the problem. This is particularly true because in several pastures along Mexican Hollow the best and thickest stands of grass were in the actual drainage, presumably because of the greater availability of water. In several places pastures away from the drainage were eroded and had a poor grass cover (contrast figs. 15 and 17). Thus cattle in these pastures would by necessity graze on molybdenum-enriched grass.

NIESCHWITZ SITE

The Nieschwitz site (figs. 1 and 19) has identified shallow mineralization in a tuffaceous sandstone within the Whitsett Formation. The sandstone crops out irregularly around the base of the hill on fig. 19. The area is a proposed mine site; however, no mining has occurred there yet. A large uranium tailings pond occurs 0.5 km to the west and could conceivably contribute windblown material. However, the prevailing wind is from the southeast so it is unlikely that any sources other than

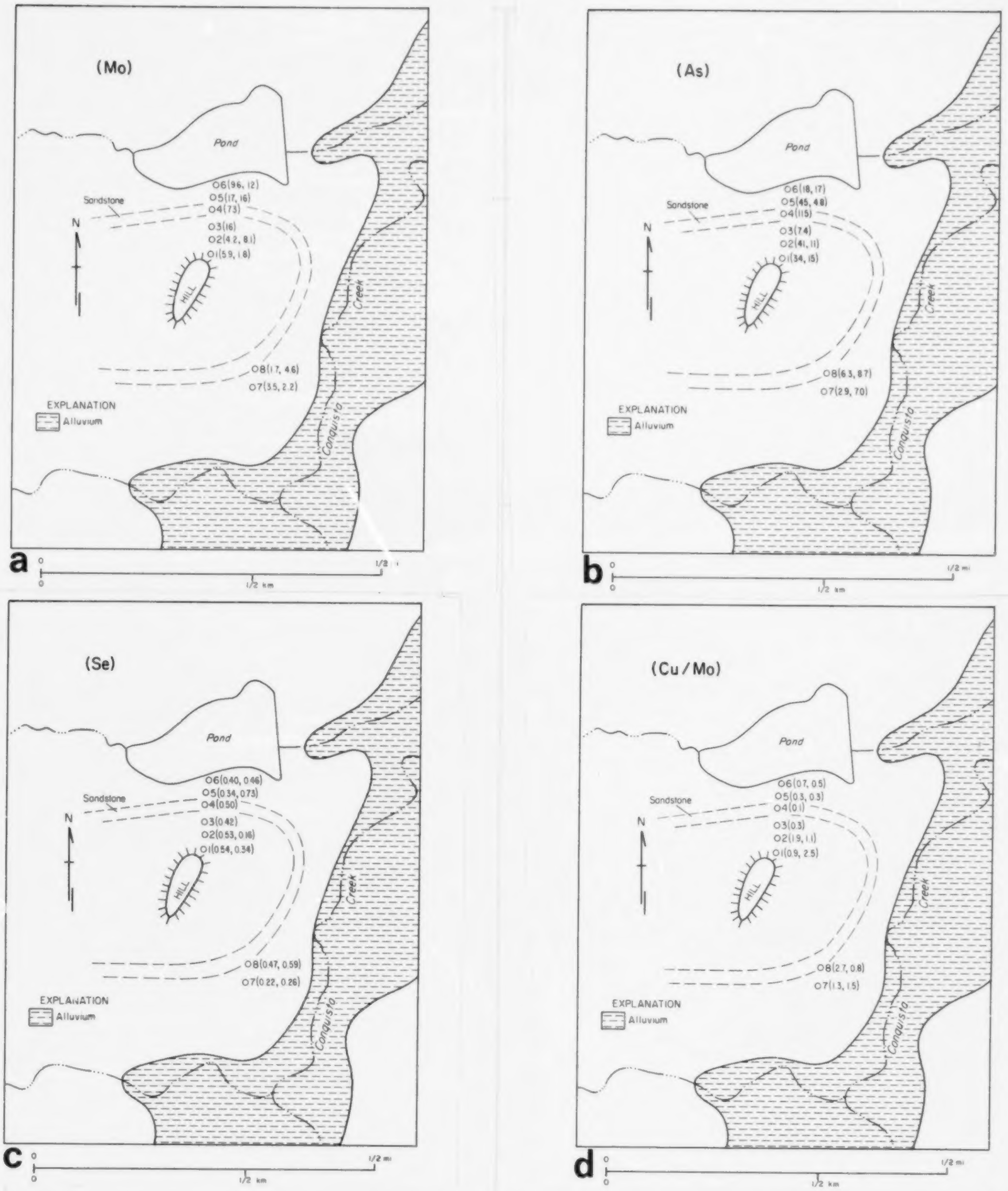
a
(Mo)
Pond
Sandstone
N
HILL
Creek
Conquista
6(96, 12)
5(17, 16)
4(73)
3(16)
2(4.2, 8.1)
1(5.9, 1.8)
8(1.7, 4.6)
7(3.5, 2.2)
EXPLANATION
Alluvium
0
1/2 mi
0
1/2 km
b
(As)
6(18, 17)
5(45, 48)
4(115)
3(7.4)
2(41, 11)
1(34, 15)
8(6.3, 8.7)
7(2.9, 7.0)
c
(Se)
6(0.40, 0.46)
5(0.34, 0.73)
4(0.50)
3(0.42)
2(0.53, 0.16)
1(0.54, 0.34)
8(0.47, 0.59)
7(0.22, 0.26)
d
(Cu/Mo)
6(0.7, 0.5)
5(0.3, 0.3)
4(0.1)
3(0.3)
2(1.9, 1.1)
1(0.9, 2.5)
8(2.7, 0.8)
7(1.3, 1.5)

Figure 19. Index map of Nieschwitz site showing sample locations (circles), mineralized sandstone, top of hill, and stock pond. Outcrop of sandstone from Brown and others (1961). Concentrations of various elements in ppm or copper/molybdenum ratio follow sample locations. First value is from A horizon; second from B horizon. (a) Molybdenum (b) Arsenic (c) Selenium (d) Copper/molybdenum ratio.

natural ones contribute to molybdenum, arsenic, or selenium concentrations at the Nieschwitz site.

Six locations were sampled in a traverse approximately north-south across the outcrop (fig. 19 and Table A-2). A and B horizons were sampled at all but locations 3 and 4. Sample 4 is from the outcrop (fig. 20) and bedrock was encountered at approximately 30 cm at location 3, so no B horizon sample was collected. Additionally, two more locations (7 and 8; A and B horizons) were sampled where the sandstone crops out on the south side of the hill.

Comparisons for anomalous concentrations are made with the Whitsett (Fashing) concentrations because the Nieschwitz site is within Whitsett outcrop even though it is also within the Falls City quadrangle. Seven out of 14 samples have molybdenum concentrations greater than the upper limit of the expected range. The highest concentration is in sample 4 (73 ppm) from the outcrop; the next highest concentrations are from sample 3 (16 ppm), a thin soil directly on top of the sandstone, and from samples 5A (17 ppm) and 5B (16 ppm), which are immediately below the sandstone outcrop. Other concentrations decrease away from the outcrop. Clearly, all concentrations are natural and related to mineralization in the sand. Molybdenum concentrations of several samples, including those from the area of outcrop on the south side of the hill, are less than the upper limit. However, all concentrations are relatively high and confirm the observation that soils developed in areas of mineralized Whitsett sandstones are enriched in molybdenum.

Arsenic concentrations correlate moderately well with molybdenum. However, the correlation coefficient of 0.87 (table A.4) is controlled at least partly by the high arsenic and molybdenum concentration of the one outcrop sample (number 4, 115 ppm arsenic). Seven out of the 14 samples have arsenic concentrations above the outlier limits but of these only 4 also have anomalous molybdenum concentrations.

Selenium concentrations do not correlate with molybdenum (table A.4). The selenium concentrations are similar to those of the Whitsett (Fashing) background samples and within the expected range. Apparently selenium was not as enriched by mineralization as was molybdenum.

Copper concentrations show no relation to mineralization or correlation with molybdenum, arsenic or selenium; all but one (2B, 8.5 ppm) are less than the upper limit. The molybdenum-copper correlation coefficient of 0.34 (table A.4) is determined almost entirely by sample 4A. Eliminating sample 4A would reduce the already low correlation of copper and molybdenum. Copper/molybdenum ratios in soil are consistently low. More than half of the samples have ratios less than one and only two exceed two.

CULPEPPER AND LYSSY SITES

Twelve samples were collected from eight locations along a strike section of the Whitsett outcrop at the Culpepper site (figs. 1 and 21; table A-2). Six samples (A horizons only) were collected from the Lyssy site (fig. 1 and 9). Both areas are sites of suspected shallow mineralization and both have moderate radioactivity anomalies (Brown and others, 1961; Eargle and Moxham, 1961). No mining has occurred at either site although the Lyssy site is within 0.5 km of older mining.

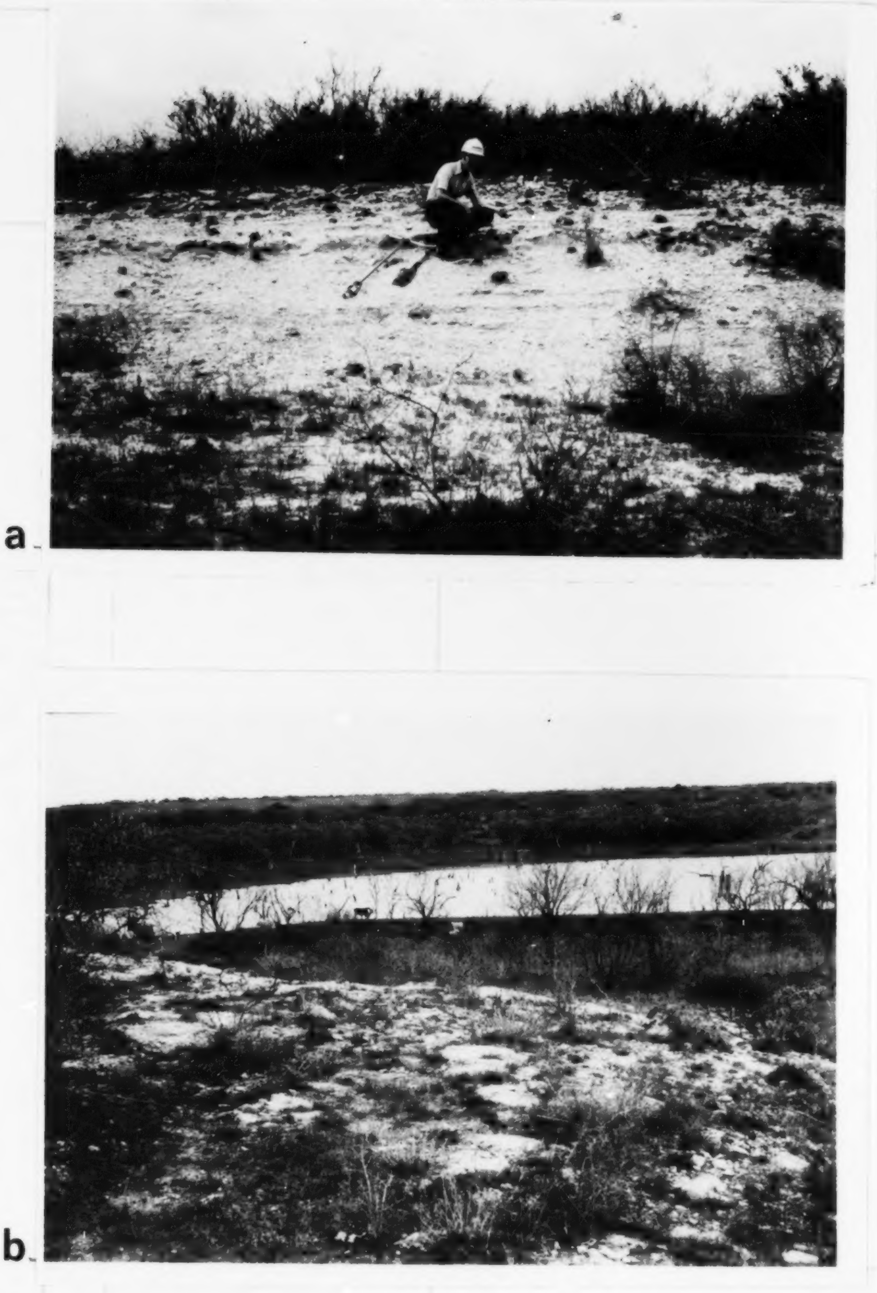

Figure 20. (a) Outcrop of sandstone at Nieschwitz site at sample location 4. (b) Outcrop of sandstone. Photographer looking north over stock pond. Sample locations 5 and 6 are between outcrop and pond.

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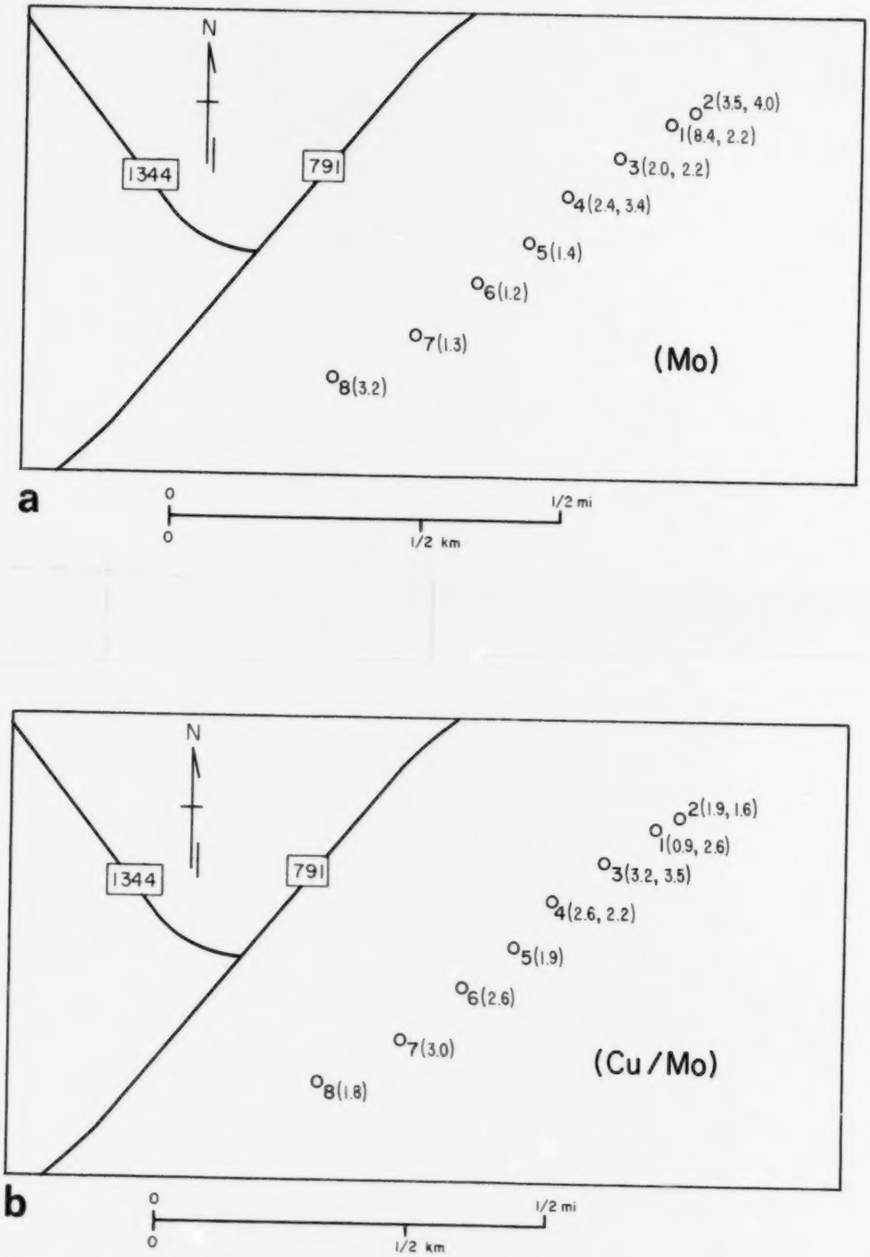
N
1344
791
2(3.5, 4.0)
1(8.4, 2.2)
3(2.0, 2.2)
4(2.4, 3.4)
5(1.4)
6(1.2)
7(1.3)
8(3.2)
(Mo)
a
0
1/2 mi
0
1/2 km
N
1344
791
2(1.9, 1.6)
1(0.9, 2.6)
3(3.2, 3.5)
4(2.6, 2.2)
5(1.9)
6(2.6)
7(3.0)
(Cu/Mo)
8(1.8)
b
0
1/2 mi
0
1/2 km

Figure 21. Index map of Culpepper site showing ranch roads and sample locations (dots). Molybdenum concentrations in ppm or copper/molybdenum ratio follow sample locations. (a) Molybdenum (b) Copper/molybdenum ratio. First value is from A horizon; second (where given) is B horizon.

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Two samples from the Lyssy site (2, 6.8 ppm; 6, 12 ppm) and one from the Culpepper site (1A, 8.4 ppm) have molybdenum concentrations greater than the expected range. The concentrations are not as high as some from other mineralized areas (for example, the Nieschwitz or Boso sites). Otherwise, molybdenum concentrations are similar to those of Whitsett (Fashing) samples.

Copper concentrations of all the Culpepper samples are within the expected range. However, three of the six Lyssy samples have copper concentrations greater than the upper limit. Possibly, the expected range for copper determined from the Whitsett (Fashing) samples is not representative of the Lyssy samples. Copper/molybdenum ratios are uniformly low. All but one are less than 5 and seven samples have ratios less than 2.

BOSO SITE

Trace element concentrations in soils and other surface materials in the vicinity of the Boso site may have a complex origin. The area is the site of both shallow mineralization and mining. The Deweesville Sandstone Member of the Whitsett Formation hosts mineralization discovered in 1954 by an aeroradioactivity survey, the initial discovery in the South Texas uranium district (Bunker and MacKallor, 1973). An aeroradioactivity map of the Fashing quadrangle shows a distinct radioactivity anomaly centered around the sampled area (Eargle and others, 1961; Moxham and Eargle, 1961; MacKallor and others, 1962). Molybdenum minerals have been identified from the Boso deposit, including jordisite, ilsemannite, iriginite (a uranyl-molybdate), and another unidentified uranyl-molybdate (Bunker and MacKallor, 1973).

Mining of the Boso deposit first occurred in 1958 with extraction of 8 to 9 tons of ore averaging more than 2 percent uranium from under only a few feet of overburden (Bunker and MacKallor, 1973). The area now has irregular mounds of spoil and sandstone and is partly overgrown with scrub vegetation. No actual pit was excavated for this early mining. This area is identified as the disturbed area on figure 22. Additional mining occurred in 1965 and produced the pit shown in figure 22. The pit at present is only about 4 m deep. There has been no reclamation of the area. However, a new mine has been proposed at the site and reclamation will occur after this mining.

Twenty-three samples were collected from 13 locations along 2 traverses across the Boso area (fig. 1 and 22; table A-2). All samples were analyzed for molybdenum, arsenic, selenium, and copper. Most of the samples have molybdenum, arsenic, and selenium concentrations above the upper limits, and with only a few exceptions samples which have high concentrations of one element also have high concentrations of the other two. Remarkably high concentrations of the elements (table A-2) occur in several samples of spoil (locations 8 and 11; Mo = 11,200, Se = 15, As = 482; Mo = 548, Se = 4.6, As = 417), of surficial material in the disturbed area (location 3; Mo = 369, Se = 16, As = 272), and of weathered bedrock beneath soil (sample 7B; Mo = 856, Se = 3.8, As = 450). In general, the samples with the highest concentrations are spoil or bedrock material. The soil samples have high concentrations (several tens of ppm Mo) but not as high as the bedrock samples. Soil samples 2A and 2B are exceptions; they have two of the highest selenium concentrations (9.1 and 14 ppm), although their molybdenum and arsenic concentrations are similar to those of other anomalous soils.

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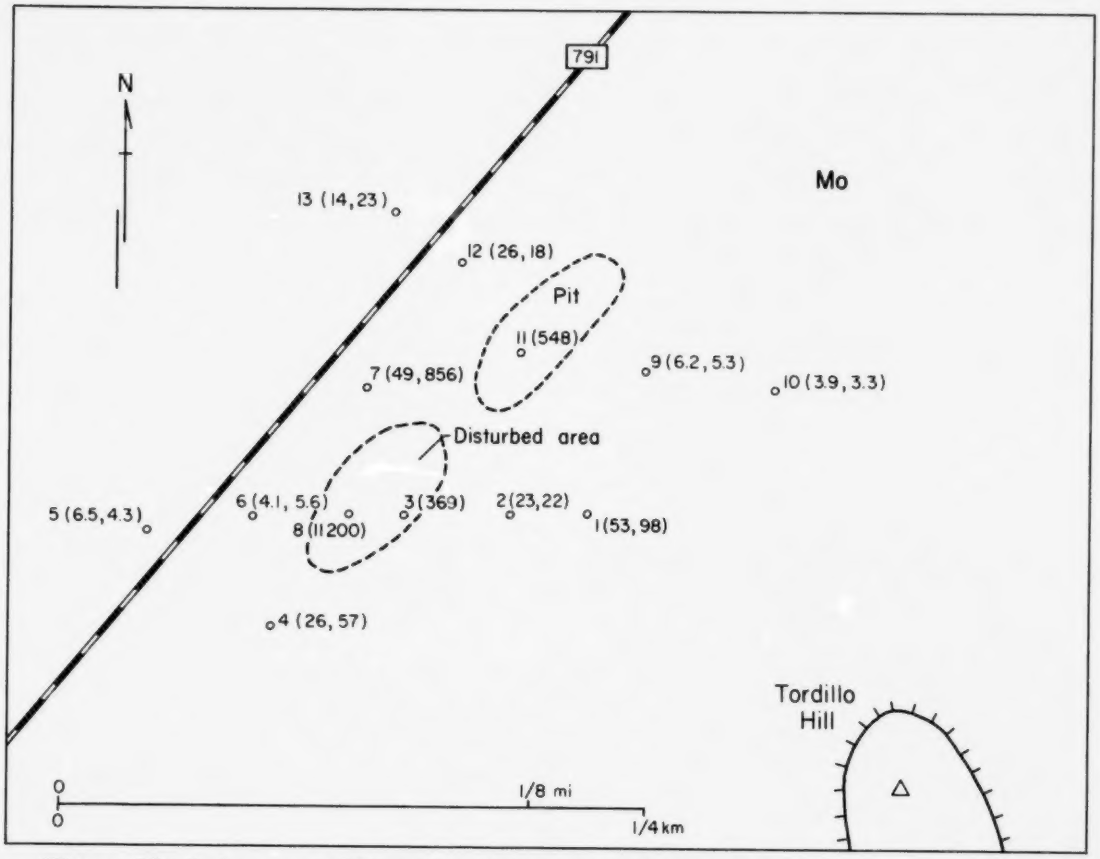

Figure 22. Index map of Boso site showing sample locations (circle), mine pit and disturbed area, and Tordillo Hill.

Copper concentrations of 10 samples are greater than the upper limit of 8.39 ppm (table A-2). None of these 10 samples are of mineralized material; all mineralized samples have lower copper concentrations. The relatively high copper concentrations suggest that the background concentrations for Whitsett (Fashing) are not representative of the Boso area. Copper/molybdenum ratios are uniformly low with only three greater than 2. Most samples have ratios much less than 1.

Because there is both natural shallow mineralization and a history of mining, the effects of either on trace elements concentrations are difficult to evaluate. Because the mineralization is shallow and uranium minerals are found in the outcrop, it is almost certain that there were naturally high concentrations of molybdenum, arsenic, and selenium in the soils before mining. However, disruption of the surface and exposure of material exceptionally rich in the trace elements may have increased the concentrations of these elements in soils that already had anomalous concentrations, or increased the total area of high concentrations. The area was investigated as a probable example of the highest concentrations. The fact that near-surface mineral-

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ization, radioactivity anomalies, and mining occur in several places along the outcrop belt of the Deweesville Sandstone suggests that other areas also have high concentrations of molybdenum, arsenic, and selenium.

TORDILLO CREEK

Tordillo Creek drains several areas which could contribute high molybdenum concentrations to soils in its channel. The drainage area in general is within the Whitsett Formation (figs. 1 and 23). Several areas of mining and shallow mineralization and one abandoned mill site are also within the drainage area (fig. 23). Finally, the one documented case of molybdenosis occurred in a pasture within the drainage area, just southeast of the mine and mill area (Dollahite and others, 1972).

Specific source areas include an abandoned mine and mill site (fig. 23) near which the confirmed molybdenosis occurred, the Boso area and several other areas of shallow mineralization (figs. 22 and 23), and the Weddington mining area (figs. 9 to 12) in addition to the general Whitsett outcrop area. Unfortunately, several important areas could not be sampled because individual landowners would not allow access.

Seven soil samples were collected from four locations near an abandoned tailings pond (S-1 through S-4). One sample from the tailings (S-5) contains 40 ppm molybdenum and 1 ppm selenium, so drainage from or erosion of the tailings should have a noticeable effect on concentrations of the two elements in nearby soils. Locations S-1 and S-2 are in a divide area that could receive windblown material from the tailings; locations S-3 and S-4 are in a drainage from the tailings area. The drainage here is not to Tordillo Creek. Molybdenum and selenium concentrations of all the soil samples are less than the upper limits. Molybdenum concentrations in particular are some of the lowest observed in soils developed on the Whitsett Formation. Samples S-3A, 3B, and 4A from the small drainage adjacent to the tailings have slightly higher molybdenum concentrations than samples 1 and 2 from the divide. Location S-4 contained debris which clearly was derived from the tailings pond embankment. Thus some material and molybdenum probably has been added to the drainage by runoff from the tailings pond; however, the amount added is small and does not exceed the background in the overall area. Windblown transport has apparently not affected molybdenum or selenium concentrations.

Ten soil samples were collected from six locations within Tordillo Creek or its tributaries and analyzed for molybdenum and copper (table A-2). Samples of Bermuda grass were collected at two of these locations. Also, sample 24 from the Weddington area is from a drainage to Tordillo Creek (figs. 9 to 12 and 23).

Interpretation of the results is complicated by the complexity and distribution of potential sources. Molybdenum concentrations of only two samples (1B, 8.3 ppm; 6B, 6.8 ppm) are greater than the expected range. Runoff from mining and mill sites has undoubtedly contributed to molybdenum concentrations in the drainages, but it is impossible to determine the relative contributions of natural and mining-related sources.

Copper concentrations in the Tordillo samples range from 2.6 to 10 ppm and show no correlation with molybdenum concentrations. Only the sample with 10 ppm copper has a concentration greater than the upper limit for copper. Copper/molyb-

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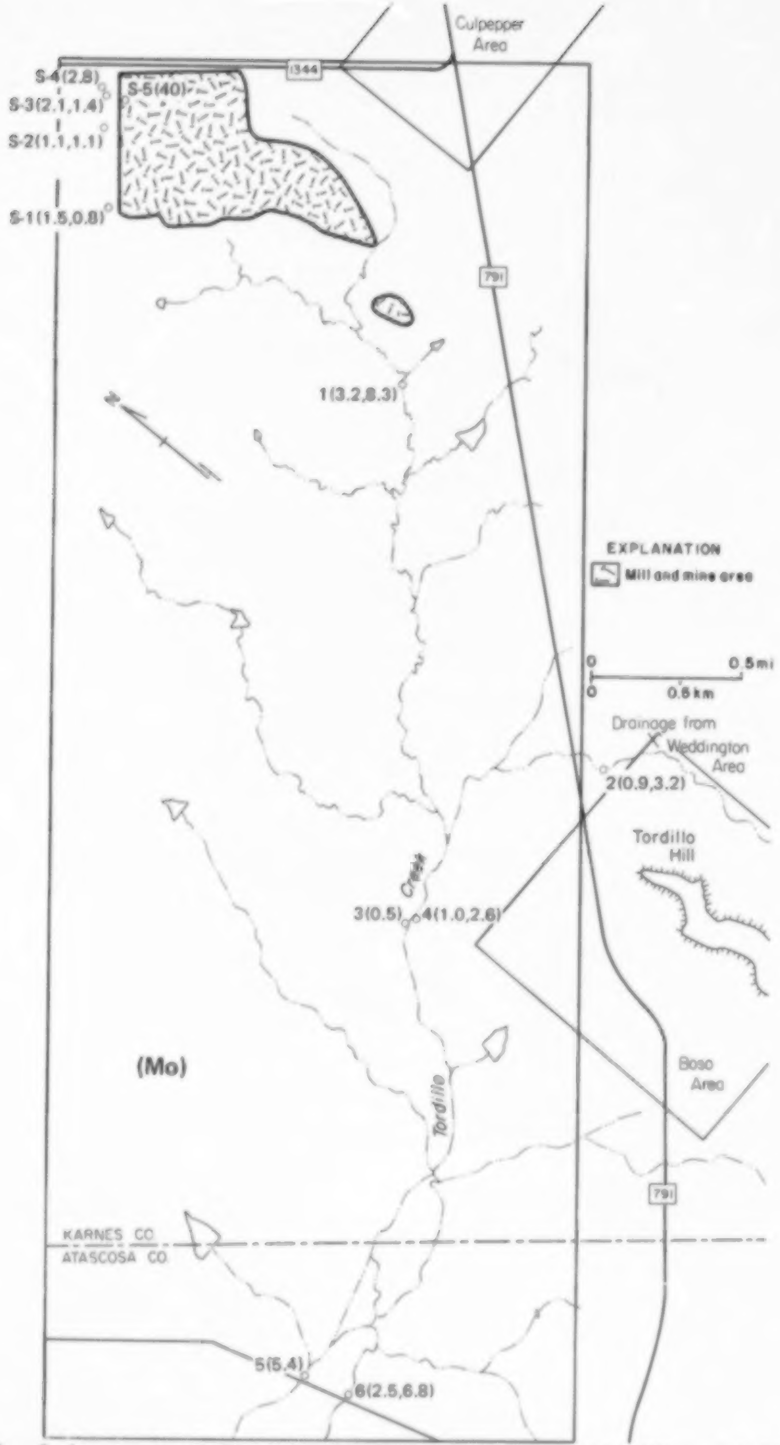
Culpepper Area
1344
S-4(2.8)
S-5(40)
S-3(2.1,1.4)
S-2(1.1,1.1)
S-1(1.5,0.8)
791
1(3.2,8.3)
N
EXPLANATION
Mill and mine area
0 0.5mi
0 0.8km
Drainage from Weddington Area
2(0.9,3.2)
Tordillo Hill
Creek
3(0.5)
4(1.0,2.6)
(Mo)
Tordillo
Boso Area
791
KARNES CO.
ATASCOSA CO.
5(5.4)
6(2.5,6.8)

Figure 23. Index map of Tordillo Creek area showing Tordillo and SW sample locations, mine and mill area, and outlines of Culpepper and Boso sites.

denum ratios in the soils range from 0.4 to 5.2. Copper concentrations of two grass samples are very similar; however, molybdenum concentrations differ by a factor of four (2C, 9.8 ppm molybdenum, 10 ppm copper; 6C, 2.5 ppm molybdenum, 8.8 ppm copper). Significantly, the grass sample with the higher molybdenum concentration comes from the soil with the lower molybdenum concentration even though pH of the soils is similar. Some other factor must be controlling availability of molybdenum. Copper/molybdenum ratios in the grass samples are 1.0 and 3.5.

The present sampling did not reveal concentrations as high as were found in Mexican Hollow. However, it does show that there are moderately high molybdenum concentrations in many of the soils, similar to concentrations found in soils of the Whitsett outcrop. Also, copper concentrations are low, and copper/molybdenum ratios in both soils and grass are low. For these reasons and because there are so many potential sources for high molybdenum, arsenic, and selenium concentrations in the drainage area of Tordillo Creek, the area should be sampled more thoroughly.

SECTION 7

CONCLUSIONS

Several of the conclusions listed here are already discussed in the body of the report and are restated only briefly. Other conclusions are stated for the first time. Many of the results are specific to the South Texas uranium mining area, but many are also applicable to environmental geochemical studies in general.

1. The stratified random sampling design used seems particularly effective in determining baseline characteristics, a critical requirement of many environmental studies. Using this procedure requires first recognizing natural variations. A geologic subdivision of the sampling design is most effective because excellent geologic mapping is available that is based on natural variation and because soil characteristics are largely derived from geologic characteristics. Further subdivision of the geologic formations used in this study (for example, the members of the Whitsett Formation) could be used to recognize additional geologically distinct environments but such subdivision would be difficult because of the members' small and irregular outcrop areas. A purely geographic subdivision of the entire uranium mining area could easily have missed some of the distinctive geochemical environments recognized, although the results would have been statistically valid.

2. The background sampling shows that soils developed on different geologic formations and even on different parts of individual formations are geochemically distinct. Trace element concentrations in soils are determined by concentrations in the parent geologic substrate. The variations in substrate composition are probably a function of original content and degree of alteration of volcanic ash and presence and intensity of uranium mineralization. Use of baseline concentrations and evaluation of the effects of mining, or of possible anomalies in areas of shallow mineralization, must recognize the natural variations.

Soils developed on the Catahoula Formation and Oakville Sandstone and some soils developed on clay-rich parts of the Whitsett Formation away from mineralized sands have molybdenum, arsenic, and selenium concentrations similar to those of published averages. Soils developed on or adjacent to mineralized sands of the Whitsett Formation have distinctly higher molybdenum concentrations; selenium concentrations are also higher, but the pattern is not as well established as for molybdenum. Because the Whitsett Formation was sampled in only one quadrangle in an area of mineralization, characterization of the formation beyond that area is not justified. Arsenic concentrations are not generally anomalous, but there are fewer data. Higher molybdenum, arsenic, or selenium concentrations could occur in mineralized areas within the Catahoula Formation and Oakville Sandstone but with the exception of the Oakville Sandstone near the Felder mining area no such areas were discovered in this study. Copper concentrations in general are low compared to published averages and are apparently lowest in areas with the highest molybdenum concentrations.

3. Sampling of mined and mineralized areas show that high to very high concentrations of molybdenum, arsenic, and selenium exist in three settings: (A) in areas of shallow mineralization, (B) in drainages adjacent to older, abandoned mines, and (C) in some reclaimed areas. High concentrations have not apparently resulted from wind transport.

A. In several areas of shallow oxidized mineralization (for example, Nieschwitz and Boso sites) concentrations of several tens of ppm molybdenum and arsenic and up to 14 ppm selenium occur naturally in soils. Higher concentrations up to several hundred ppm molybdenum and arsenic (and one sample with 11,000 ppm molybdenum) occur in near-surface material exposed by mining. However, probably no natural soils have concentrations that high.

Several other areas of possible shallow mineralization (for example, Culpepper and Lyssy) have moderately high molybdenum concentrations, but most concentrations are not anomalous in comparison to background concentrations. This simply confirms the observation that soils developed on mineralized parts of the Whitsett Formation have generally high molybdenum concentrations.

Other possible locations with naturally high concentrations of the trace elements are not abundant in the area of this study. Sands of the Oakville Sandstone at the Felder site have slightly anomalous molybdenum concentrations. However, background concentrations from the random sampling are uniformly low, and there is no other evidence to suggest that high concentrations are extensive in the Oakville Sandstone. Shallow mineralization is not abundant in either the Oakville Sandstone or the Catahoula Formation in this area. Naturally high concentrations of the trace elements should not be common in soils developed on them. However, high concentrations could exist if shallow mineralization, similar to that in the Whitsett Formation, is present in other areas.

B. High concentrations of trace elements exist in several mining areas and result from waterborne transport of suspended or dissolved material from the mining areas. Two processes may in part be responsible: (1) Prior to about 1973, water which accumulated in the pits either from ground-water discharge or surface-water runoff was routinely pumped into adjacent drainages for disposal. (2) Erosion of abandoned spoil piles has washed overburden into the heads of several drainages, and runoff from the spoil piles could carry either dissolved or suspended trace elements.

C. Only a few samples of soil and overburden in reclaimed areas were collected. One soil sample in a reclaimed area and two samples of overburden under a thin cover of restored topsoil have high molybdenum (or selenium) concentrations. The total extent of the high concentrations in reclaimed areas is not known and may be small, but the distribution of concentrations shows that some mechanism can transfer trace elements from overburden to overlying reclaimed topsoil. Physical mixing is one mechanism but was not responsible for the higher concentration of all samples. Purely chemical transport by soil moisture is also likely.

4. Measurable increases in trace element concentrations in soils adjacent to mining areas have apparently not occurred by wind transport of overburden. Concen-

trations of the trace elements in soils upwind and downwind of mining areas that were unreclaimed and unrevegetated for many years (and thus should be highly susceptible to wind erosion) are similar to each other and to background concentrations. This is despite the fact that South Texas is semiarid and prone to wind erosion. Also, at several times during sampling, windblown dust could be seen arising from spoil piles and being transported to the northwest, so wind erosion is occurring. The fact that no measurable concentration differences were found may be because molybdenum and other element concentrations in most of the overburden are not particularly high and the total volume of wind blown material is small relative to the area affected. Also much of the mineralized material consists of relatively coarse sand which should be less susceptible to wind transport.

Certain aspects of wind transport were not evaluated. One landowner suggested that wind transported dust could coat grass and be consumed with the grass. No sampling to evaluate the effects of this kind of wind transport was made. At best, it can be stated that it has not measurably affected concentrations on related soils.

Also, little sampling was done around uranium mill sites where wind transport might be more likely because tailings and stockpiled ore provide relatively easily erodable material with high trace element concentrations. Several samples collected at one abandoned mill site show no discernible effects of wind transport. Additional sampling at the one active and the other abandoned mill sites would be useful nevertheless.

5. Copper/molybdenum ratios in Bermudagrass collected both from the background soils and from soils in mining areas are low, with ratios of all but three samples less than 5. Two of the high ratios are due to anomalously high copper concentrations which are probably not representative of grass throughout the area. The low ratios result from both high molybdenum concentrations in some grass samples and from low copper concentrations in other samples. Grass samples with high molybdenum concentrations are from channels draining mining or mineralized areas; high molybdenum concentrations in the soils in the channels result from runoff from the mining areas. Grass with low copper concentrations occurs on background soils with normal molybdenum concentrations but low copper concentrations. Thus, both contaminated and normal soils have low ratios although the lowest ratios (less than one) are from soils affected by mine drainage.

With four exceptions, the copper/molybdenum ratio in grass is less than the ratio in the associated soil. This probably reflects the high availability of molybdenum and low availability of copper in the high pH, poorly drained soils of the uranium mining area. The few exceptions include two grass samples with inexplicably high copper concentrations and two samples from soils with relatively low pH, in which copper may be relatively more available.

All but three of the measured ratios in grass are below what is considered optimum (6 or 7) and similar to ratios in forage which have been implicated in molybdenosis (Dollahite and others, 1972; Alloway, 1973). Thus, molybdenosis in the uranium mining area could potentially result both from natural and mining-related processes. Drainage from mining areas could have markedly aggravated a natural situation by sharply increasing local molybdenum concentrations in soil.

The numerous soil and few grass analyses suggest that large parts of the uranium mining region could have grass with copper/molybdenum ratios less than optimum and potentially low enough to cause molybdenosis in cattle. This results because natural soils have normal to high molybdenum concentrations (1 to 5 ppm) and low copper concentrations (10 ppm or less) and because molybdenum is more available to plants than is copper in these soils. Most reports of molybdenosis have been concentrated in a few areas near mining centers and are not apparently widespread away from mining areas, however. The explanation of this discrepancy is not certain. Four possibilities are (1) available grass analyses are not representative, (2) some other factors (such as copper supplements to feed or rotation of herds onto different pastures) are checking the occurrence of molybdenosis, (3) molybdenosis has occurred but has not been recognized, or (4) copper/molybdenum ratios less than 6 in grass may not be critical. A possible mediating factor is that the soils with the highest molybdenum and lowest copper concentrations generally have lowest pH (for example, soils developed on the Whitsett Formation). In these soils copper may be relatively more available and molybdenum less so. Nevertheless, the results suggest a potentially significant natural problem which should be carefully checked.

RECOMMENDATIONS

An immediate need is a thorough inventory of areas that are likely to have high molybdenum concentrations, including areas of near-surface mineralization and areas which have received mine drainage. Areas of near-surface mineralization can be identified from radioactivity anomalies. Because of the intense exploration for uranium in South Texas, there are several published aeroradioactivity surveys. Soil and grass sampling in these areas should show the extent of areas rich in natural molybdenum, arsenic, or selenium.

Areas which have received mine drainage also should be investigated. Mine drainage includes both runoff from abandoned spoil piles and pit water pumped out of the mines during dewatering. It is possible and even likely that both processes have contributed to increased molybdenum concentrations in soils in adjacent drainages. However, it would be worthwhile to attempt to evaluate relative contributions. Although mine water once discharged into the drainages cannot now be sampled, water occurring now in pits can be sampled. Water from pits that have been abandoned and leached for many years may not be representative of water discharged during mining, however. Because pit water was routinely discharged into local streams until the early 1970's, many streams may have been contaminated.

Runoff water from abandoned spoil piles can be analyzed to see whether molybdenum or other trace elements are being contributed to the drainages at present. Attempts to deal with the high concentrations in contaminated areas must first shut off presently active sources. Systematic sampling of streams adjacent to areas of older mining and draining areas of shallow mineralization is necessary.

Reclaimed areas should be surveyed to determine the extent of high concentrations in reclaimed topsoil and in overburden immediately beneath the topsoil. Also the mechanism of trace element transfer from overburden to soil needs to be determined to evaluate the possibility of long-term problems. Identification and isolation of overburden rich in molybdenum, arsenic, or selenium is presently required by surface mining regulations. However, most trace element-rich overburden is near the ore zone and is the last material to be removed from the mine pit. Thus, it is difficult to place this material beneath previously extracted overburden that is not trace element rich. A survey of reclaimed areas would show whether burial by topsoil only is sufficient to prevent surface contamination, or whether deeper burial under overburden that is not trace element rich is necessary.

Analysis of grass and other vegetation from the above areas and also from areas of presumed normal molybdenum concentrations in soil is necessary to document the extent of grass with low copper/molybdenum ratios. Investigation of availability tests to determine which are appropriate to the soils of the region and application in the area would be useful to determine uptake not only of molybdenum but also of arsenic and selenium.

This study presents data on the natural distribution of molybdenum, copper, arsenic, and selenium, and an evaluation of the effects of some of man's activities. However, the significance of different trace element concentrations in soil and forage is poorly understood. The South Texas area could be an effective laboratory to document natural variations in uptake and to evaluate their significance. For example, blanket copper supplementation to cattle feed in the area could alleviate potential problems of molybdenosis. However, the degree to which copper supplementation is effective is uncertain. Treatment may be effective in minor imbalances of copper and molybdenum but not in greater imbalances. Study of the South Texas area could help answer such fundamental questions.

REFERENCES

Allaway, W. H., 1977, Perspectives on molybdenum in soils and plants, *in* Chappell, W. R., and Petersen, K. K., eds., Molybdenum in the environment, v. 2, p. 317-339.

Allcott, G. H., and Lakin, H. W., 1974, Statistical summary of geochemical data furnished by 85 laboratories for six geochemical exploration reference samples: U.S. Geological Survey Open-File Report, 103 p.

Alloway, B. J., 1973, Copper and molybdenum in swayback pastures: Journal of Agricultural Science, v. 80, p. 521-524.

Anderson, R. L., and Bancroft, T. A., 1952, Statistical theory in research: New York, McGraw-Hill, 399 p.

Anderson, B. M., Keith, J. R., and Connor, J. J., 1975, Antimony, arsenic, germanium, lithium, mercury, selenium, tin, and zinc in soils of the Powder River Basin, *in* U.S. Geological Survey Open-File Report 75-436, p. 50-57.

Arbingast, S. A., Kennamer, L. G., Ryan, R. H., Lo, A., Korney, D. L., Zlatkovich, C. P., Bonine, M. E., and Steele, R. G., 1973, Atlas of Texas: The University of Texas at Austin, Bureau of Business Research, 132 p.

Barnes, V. E., 1976, Crystal City-Eagle Pass Sheet: The University of Texas at Austin, Bureau of Economic Geology, Geologic Atlas of Texas, scale 1:250,000.

Barrow, N. J., 1977, Factors affecting the molybdenum status of soils, *in* Chappell, W. R., and Petersen, K. K., eds., Molybdenum in the environment, v. 2, p. 583-595.

Boyle, R. W., and Jonasson, I. R., 1973, The geochemistry of arsenic and its use as an indicator element in geochemical prospecting: Journal of Geochemical Exploration, v. 2, p. 251-296.

Bremner, J. M., 1965, Inorganic forms of nitrogen, *in* C. A. Black, ed., Methods of Soil Analyses, Part 2: Madison, Wisconsin, The American Society of Agronomy, Inc., Agronomy Series No. 9, p. 1196.

Brown, R. D., Eargle, D. H., and Moxham, R. M., 1961, Preliminary aeroradioactivity and geologic map of the Falls City N. E. quadrangle, Karnes and Wilson Counties, Texas: U.S. Geological Survey Geophysical Investigations Maps GP-250.

Bunker, C. M., and MacKallor, J. A., 1973, Geology of the oxidized uranium ore deposits of the Tordillo Hill-Deweesville area, Karnes County, Texas—A study of a district before mining: U.S. Geological Survey Professional Paper 765, 37 p.

TYPING GUIDE SHEET

Case, A. A., 1974, Toxicity of various chemical agents to sheep: Journal of American Veterinary Medicine Association, v. 164, p. 277-283.

Chappell, W. R., and Petersen, K. K., 1977, Molybdenum in the environment: New York, Marcel Dekker.

Connor, J. J., and Shacklette, H. T., 1975, Background geochemistry of some rocks, soils, plants, and vegetables in the conterminous United States: U.S. Geological Survey Professional Paper 574-F, 168 p.

Crenshaw, G. L., and Lakin, H. W., 1974, A sensitive and rapid method for the determination of trace amounts of selenium in geologic materials: Journal of Research of the U.S. Geological Survey, v. 2, p. 483-487.

Dickinson, K. A., 1975, Geologic map showing ore controls, Karnes uranium area, Texas: U.S. Geological Survey Open-File Report.

Dollahite, J. W., Rowe, L. D., Cook, L. M., Hightower, D., Bailey, E. M., and Kyzar, J. R., 1972, Copper deficiency and molybdenosis intoxication associated with grazing near a uranium mine: Southwestern Veterinarian, Fall, 1972, p. 47-50.

Eargle, D. H., Brown, R. D., Jr., and Moxham, R. M., 1961, Preliminary aeroradioactivity and geologic map of the Falls City SW quadrangle, Atascosa, Karnes, and Live Oak Counties, Texas: U.S. Geological Survey Geophysical Investigations Map 6P-252.

Eargle, D. H., Dickinson, K. A., and Davis, B. O., 1975, South Texas uranium deposits: American Association of Petroleum Geologists Bulletin, v. 59, p. 766-779.

Eargle, D. H., Hinds, G. W., and Weeks, A. M. D., 1973, Uranium geology and mines, South Texas: The University of Texas at Austin, Bureau of Economic Geology Guidebook No. 12, 61 p.

Eargle, D. H., and Moxham, R. M., 1961, Preliminary aeroradioactivity and geologic map of the Falls City SE quadrangle, Atascosa, Karnes, and Live Oak Counties, Texas: U.S. Geological Survey Geophysical Investigations Map 6P-253.

Eargle, D. H., and Weeks, A. M. D., 1968, Factors in the formation of uranium deposits, coastal plain of Texas: South Texas Geological Society Bulletin, v. 9, p. 3-13.

Erdman, J. A., Ebens, R. J., and Case, A. A., 1978, Molybdenosis: A potential problem in ruminants grazing on coal mine spoils: Journal of Range Management, v. 31, p. 34-36.

Exxon Company, U.S.A., 1976, Application for a surface mining and reclamation permit submitted to the Texas Railroad Commission, Nov. 1, 1976.

Fine, L. O., 1965, Selenium, *in* C. A. Black, ed., Methods of soil analyses, Part 2, Madison, Wisconsin, The American Society of Agronomy, Inc., Agronomy Series No. 9, p. 1117-1123.

TYPING GUIDE SHEET

Fisher, W. L., Proctor, C. V., Jr., Galloway, W. E., and Nagle, J. S., 1970, Depositional systems in the Jackson Group of Texas--their relationship to oil, gas, and uranium: The University of Texas at Austin, Bureau of Economic Geology, Geological Circular 70-4.

Galloway, W. E., 1977, Catahoula formation of the Texas Coastal Plain: Depositional systems, composition, structural development, ground-water flow history and uranium distribution: The University of Texas at Austin, Bureau of Economic Geology, Report of Investigations No. 87, 59 p.

Galloway, W. E., and Kaiser, W. R., in press, Catahoula formation of the Texas Coastal Plain: Origin, geochemical evolution, and characteristics of uranium deposits: The University of Texas at Austin, Bureau of Economic Geology, Report of Investigations.

Goldhaber, M. B. and Reynolds, R. L., 1977, Geochemical and mineralogical studies of a South Texas roll front uranium deposit: U. S. Geological Survey, Open-File Report 77-821, 34 p.

Griggs, J. L., 1953, Determination of the available molybdenum of soils: New Zealand Journal of Science and Technology, v. A34, p. 405-414.

Harshman, E. N., 1974, Distribution of elements in some roll-type uranium deposits, *in* Formation of uranium ore deposits: International Atomic Energy Agency, Vienna, p. 169-183.

Ho, C. L., and DuPont, J., 1978, Unpublished procedure: The University of Texas at Austin, Bureau of Economic Geology, Mineral Studies Laboratory.

Ho, C. L., Gonzales, R., and Tweedy, S., 1978, Unpublished procedure: The University of Texas at Austin, Bureau of Economic Geology, Mineral Studies Laboratory.

Hossner, Lloyd R., 1976, Chemical, physical, and radiometric properties of six major soil series in Live Oak County, Texas: Texas Agricultural Experimental Station, unpublished report.

Jeffery, P. G., 1970, Chemical methods of rock analysis: New York, Pergamon, p. 118.

Krumbein, W. C., and Slack, H. A., 1956, Statistical analysis of low level radioactivity of Pennsylvanian black fissile shale in Illinois: Geological Society of America Bulletin, v. 67, p. 739-762.

Kubota, J., 1977, Molybdenum status of United States soils and plants, *in* Chappell, W. R., and Petersen, K. K., eds., Molybdenum in the environment, v. 2, p. 555-581.

Lakin, H. W., 1961, Selenium content of soils, *in* Selenium in agriculture, U.S. Department of Agriculture Handbook 200, p. 27-34.

__________ 1972, Selenium accumulation in soils and its absorption by plants and animals, *in* Geological Society of America Special Paper 140, p. 45-56.

EPA-287 (Cin.)
(4-76)

__________ 1973, Selenium in our environment, *in* Kothny, E. L., ed., Advances in chemistry series (123): American Chemical Society, Washington, D.C., p. 96-111.

Langmuir, D., 1978, Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits: Geochimica et Cosmochimica Acta, v. 42, p. 547-569.

Luh, M., Baker, R. A., and Henley, D. E., 1973, Arsenic analysis and toxicity—a review, *in* The science of the total environment, v. 2, p. 1-12.

MacKallor, J. A., Moxham, R. M., Tolozko, L. R., and Popenoe, P., 1962, Radioactivity and geologic map of the Tordilla Hill-Deweesville area, Karnes County, Texas: U.S. Geological Survey Geophysical Investigations Map GP - 199.

Michael, S., and White, C. L., 1976, Fluorometric determination of submicrogram concentrations of Se in sulfide samples, Analytical Chemistry, v. 48, p. 1484-1486.

Miesch, A. T., 1976, Sampling designs for geochemical surveys-syllabus for a short course: U.S. Geological Survey Open-File Report 76-772, 140 p.

Mitchell, R. L., 1971, Trace elements in soils, *in* Technical Bulletin 21, Trace elements in soils and crops: Ministry of Agriculture, Fisheries, and Food, p. 8-20.

Moxham, R. M., 1964, Radioelement dispersion in a sedimentary environment and its effect on uranium exploration: Economic Geology, v. 59, p. 309-321.

Moxham, R. M., and Eargle, D. H., 1961, Airborne radioactivity and geologic map of the Coastal Plain area, southeast Texas: U.S. Geological Survey Geophysical Investigations Map GP-198.

National Academy of Sciences, 1976, Selenium: Committee on medical and biological effects of environmental pollutants, 203 p.

__________ 1977a, Arsenic: Committee on medical and biological effects of environmental pollutants, 332 p.

__________ 1977b, Copper: Committee on medical and biological effects of environmental pollutants, 115 p.

Nichols, C. E., Butz, T. R., Cagle, G. W., and Kane, V. E., 1977, Uranium geochemical survey in the Crystal City and Beeville quadrangles, Texas: U.S. Energy Research and Development Administration K/UR-5, 132 p.

Quin, B. F., and Brooks, R. R., 1975, The rapid colorimetric determination of molybdenum with dithiol in biological, geochemical, and steel samples: Analytica Chimica Acta 74, p. 75-84.

Ringrose, C. A., Klusman, R. W., and Dean, W. E., 1976, Geochemical variations in soils in the Piceance Creek Basin, *in* Geochemical Survey of the Western Energy Region: U.S. Geological Survey Open-File Report 76-729, p. 130-146.

Shacklette, H. T., Sauer, H. I., and Miesch, A. T., 1970, Geochemical environments and cardiovascular mortality rates in Georgia: U.S. Geological Survey Professional Paper 574-C, 39 p.

Thornton, I., 1977, Biogeochemical studies on molybdenum in the United Kingdom, *in* Chappell, W. R., and Petersen, K. K., eds., Molybdenum in the environment, New York, Marcel Dekker, v. 2, p. 341-369.

Tidball, R. R., 1975, Sampling requirements for mapping soil geochemistry in the Powder River Basin, Montana-Wyoming, *in* Geochemical Survey of the Western Coal Regions: U.S. Geological Survey Open-File Report 75-436, p. 20-28.

Tidball, R. R., Erdman, J. A., and Ebens, R. J., 1974, Geochemical baselines for sagebrush and soil, Powder River Basin, Montana-Wyoming, *in* Geochemical Survey of the Western Coal Regions: U.S. Geological Survey Open-File Report 74-250, p. 6-13.

Underwood, E. J., 1977, Trace elements in human and animal nutrition (4th ed.): New York, Academic Press.

Webb, J. S., and Atkinson, W. J., 1965, Regional geochemical reconnaissance applied to some agricultural problems in County Limerick, Eire: Nature, v. 208, p. 1056-1059.

White, W. A. and Galloway, W. E., 1977, Guide to modern barrier environments of Mustang and North Padre Islands and Jackson (Eocene) barrier/lagoon facies of the South Texas uranium district: The University of Texas at Austin, Bureau of Economic Geology, Research Note 7, 51 p.

Williams, C., and Thornton, I., 1973, The use of soil extractants to estimate plant-available molybdenum and selenium in potentially toxic soils: Plant and Soil, v. 39, no. 1, p. 149-159.

APPENDIX A: ANALYTICAL AND STATISTICAL DATA

TABLE A-1. BACKGROUND SAMPLES

Whitsett Formation
Fashing Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
N-SE-SE-EA	Tordia clay	7.9	0.7	6.6	9.4	0.06	4.7
N-SE-SE-EB	Tordia clay	8.0	0.6	7.3	12	0.02	5.6
N-SE-SE-WA	Tordia clay	7.7	1.0	5.6	5.6	0.08	5.4
N-SE-SE-WB	Tordia clay	8.0	0.9	6.1	6.8	0.01	5.4
N-SE-NW-NEA	Tordia clay	8.2	0.2	4.3	22	0.20	5.5
N-SE-NW-NEB	Tordia clay	8.2	1.9	4.4	2.3	0.16	17
N-SE-NW-SWA	Tordia clay	6.6	1.7	3.4	2.0	0.12	4.0
N-SE-NW-SWB	Tordia clay	8.1	1.4	4.8	3.4	0.13	1.8
N-SE-NW-SW	(Bermudagrass)	-	2.1	4.4	2.1	-	-
N-NW-NW-NEA	Weigang silty clay loam	7.7	2.8	4.6	1.6	0.36	9.9
N-NW-NW-NEB	Weigang silty clay loam	7.0	3.0	4.3	1.4	0.31	5.0
N-NW-NW-SWA	Weigang silty clay loam	7.5	2.5	3.5	1.4	0.28	3.6
N-NW-NW-SWB	Weigang silty clay loam	5.9	4.6	4.1	0.9	0.53	7.5
N-NW-NW-SW	(Bermudagrass)	-	2.2	5.5	2.5	-	-
N-NW-SE-NWA	Weigang silty clay loam	6.5	1.5	4.2	2.8	0.37	6.3
N-NW-SE-NWB	Weigang silty clay loam	7.9	3.0	4.4	1.5	0.53	7.9
N-NW-SE-SEA	Weigang silty clay loam	6.9	1.5	3.9	2.6	0.22	4.2
N-NW-SE-SEB	Weigang silty clay loam	8.2	4.0	5.6	1.4	0.90	4.3

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Whitsett Formation
Fashing Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
S-SE-NW-NEA	Weigang silty clay loam	7.8	2.7	5.8	2.1	0.05	6.0
S-SE-NW-NEB	Weigang silty clay loam	8.2	1.6	6.3	3.9	0.02	3.3
S-SE-NW-NE	(Bermudagrass)	-	4.0	5.1	1.3	-	-
S-SE-NW-SWA	Weigang silty clay loam	7.2	1.8	5.2	2.9	0.01	2.6
S-SE-NW-SWB	Weigang silty clay loam	8.3	3.1	6.1	2.0	0.01	6.1
S-SE-SE-NA	Weigang silty clay loam	6.4	2.4	5.9	2.5	0.31	6.8
S-SE-SE-NB	Weigang silty clay loam	6.4	2.4	5.4	2.3	0.13	6.8
S-SE-SE-SA	Weigang silty clay loam	6.4	2.5	6.1	2.4	0.25	5.9
S-SE-SE-SB	Weigang silty clay loam	6.7	2.3	4.9	2.1	0.10	2.7
S-NW-NW-NA	Monteola clay	6.6	1.9	7.2	3.8	0.04	5.7
S-NW-NW-NB	Monteola clay	7.9	2.0	8.1	4.1	0.01	4.3
S-NW-NW-SA	Monteola clay	6.8	2.1	6.3	3.0	0.09	3.1
S-NW-NW-SB	Monteola clay	7.8	2.3	6.6	2.9	0.15	2.2
S-NW-SE-NEA	Monteola clay	6.6	2.3	6.9	3.0	0.10	4.2
S-NW-SE-NEB	Monteola clay	7.6	2.3	8.3	3.6	0.06	4.0
S-NW-SE-SWA	Monteola clay	6.8	1.8	5.0	2.8	0.10	0.6
S-NW-SE-SWB	Monteola clay	7.8	2.6	5.0	1.9	0.16	5.5

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Catahoula Formation
Ecleto Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
N-W-NE-NA	Monteola clay	7.8	0.3	8.3	28	0.26	-
N-W-NE-NB	Monteola clay	7.7	0.5	20	40	0.23	-
N-W-NE-N	(Bermudagrass)	-	2.1	5.8	2.8	-	-
N-W-NE-SA	Monteola clay	7.9	2.1	6.9	3.3	0.16	-
N-W-NE-SB	Monteola clay	7.7	1.0	7.5	7.5	0.11	-
N-W-SW-NA	Monteola clay	7.8	2.1	6.6	3.1	0.16	-
N-W-SW-NB	Monteola clay	7.8	4.0	6.7	1.7	0.08	-
N-W-SW-SA	Monteola clay	7.7	1.0	9.6	9.6	0.03	-
N-W-SW-SB	Monteola clay	7.8	1.1	8.4	7.6	0.11	-
N-W-SW-S	(Bermudagrass)	-	1.7	4.2	2.5	-	-
N-E-N-EA	Monteola clay	7.9	1.2	7.5	6.3	0.10	-
N-E-N-EB	Monteola clay	7.9	2.0	9.6	4.8	0.07	-
N-E-N-WA	Monteola clay	7.8	0.8	9.5	12	0.12	-
N-E-N-WB	Monteola clay	7.9	0.7	9.8	14	0.06	-
N-E-N-W	(Bermudagrass)	-	2.1	9.7	4.6	-	-
N-E-S-NA	Monteola clay	7.4	0.8	8.8	11	0.11	-
N-E-S-NB	Monteola clay	7.9	1.1	11	9.9	0.09	-
N-E-S-SA	Monteola clay	7.7	1.0	8.1	8.1	0.10	-
N-E-S-SB	Monteola clay	7.9	0.9	10	11	0.06	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Catahoula Formation

Ecleto Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
S-SW-W-NA	Tordia clay	6.7	1.9	3.4	1.8	0.11	-
S-SW-W-NB	Tordia clay	5.1	1.4	5.8	4.1	0.23	-
S-SW-W-SA	Tordia clay	6.9	1.6	2.9	1.8	0.12	-
S-SW-W-SB	Tordia clay	5.6	0.8	5.4	6.8	0.60	-
S-SW-E-NWA	Tordia clay	6.0	2.0	3.3	1.7	0.12	-
S-SW-E-NWB	Tordia clay	4.9	1.5	7.6	5.1	0.58	-
S-SW-E-SEA	Tordia clay	6.0	1.0	5.1	5.1	0.32	-
S-SW-E-SEB	Tordia clay	6.7	0.8	6.8	8.5	0.33	-
S-NE-NW-NA	Monteola clay	7.8	0.8	13	16	0.13	-
S-NE-NW-NB	Monteola clay	7.8	0.7	7.0	10	0.06	-
S-NE-NW-SA	Monteola clay	7.9	0.6	8.1	14	0.12	-
S-NE-NW-SB	Monteola clay	8.0	0.6	7.2	12	0.07	-
S-NE-SE-NWA	Monteola clay	8.0	0.5	7.5	15	0.09	-
S-NE-SE-NWB	Monteola clay	8.2	0.5	7.2	14	0.04	-
S-NE-SE-NW	(Bermudagrass)	-	0.9	6.9	7.7	-	-
S-NE-SE-SEA	Monteola clay	7.8	0.5	7.9	16	0.13	-
S-NE-SE-SEB	Monteola clay	8.1	0.3	7.4	25	0.03	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Catahoula Formation

Falls City Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
E-SW-NW-NA	Pawelek clay loam	6.8	0.9	-	-	0.10	-
E-SW-NW-NB	Pawelek clay loam	7.9	0.6	-	-	0.12	-
E-SW-NW-SA	Pawelek clay loam	7.2	0.7	-	-	0.18	-
E-SW-NW-SB	Pawelek clay loam	7.8	0.7	-	-	0.14	-
E-SW-SE-NEA	Pawelek clay loam	7.1	0.9	-	-	0.10	-
E-SW-SE-NEB	Pawelek clay loam	7.4	0.7	-	-	0.26	-
E-SW-SE-SWA	Pawelek clay loam	7.4	0.8	-	-	0.18	-
E-SW-SE-SWB	Pawelek clay loam	7.6	0.5	-	-	0.01	-
E-NE-NE-NEA	Monteola clay	6.9	0.6	-	-	0.22	-
E-NE-NE-NEB	Monteola clay	7.5	0.7	-	-	0.14	-
E-NE-NE-SWA	Monteola clay	6.8	0.7	-	-	0.26	-
E-NE-NE-SWB	Monteola clay	7.5	0.6	-	-	0.20	-
E-NE-SW-NA	Monteola clay	7.0	0.9	-	-	0.29	-
E-NE-SW-NB	Monteola clay	7.6	0.2	-	-	0.22	-
E-NE-SW-SA	Monteola clay	6.3	0.5	-	-	0.20	-
E-NE-SW-SB	Monteola clay	7.7	0.4	-	-	0.18	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Catahoula Formation
Falls City Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
W-N-NW-WA	Monteola clay	7.8	1.0	-	-	0.18	-
W-N-NW-WB	Monteola clay	8.0	1.0	-	-	0.22	-
W-N-NW-EA	Monteola clay	7.9	0.9	-	-	0.15	-
W-N-NW-EB	Monteola clay	7.9	0.8	-	-	0.16	-
W-N-SE-WA	Monteola clay	7.3	0.8	-	-	0.20	-
W-N-SE-WB	Monteola clay	8.1	0.9	-	-	0.30	-
W-N-SE-EA	Monteola clay	7.9	0.8	-	-	0.27	-
W-N-SE-EB	Monteola clay	7.6	0.8	-	-	0.22	-
W-S-NE-NWA	Monteola clay	7.9	1.0	-	-	0.30	-
W-S-NE-NWB	Monteola clay	8.0	0.4	-	-	0.13	-
W-S-NE-SEA	Monteola clay	7.9	0.5	-	-	0.17	-
W-S-NE-SEB	Monteola clay	8.0	0.6	-	-	0.06	-
W-S-SW-NEA	Monteola clay	7.8	0.6	-	-	0.19	-
W-S-SW-NEB	Monteola clay	8.1	0.4	-	-	0.08	-
W-S-SW-SWA	Monteola clay	7.1	0.6	-	-	0.14	-
W-S-SW-SWB	Monteola clay	7.8	0.7	-	-	0.14	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

Table A-1. (continued)

Catahoula Formation
Coy City Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
N-W-SW-NEA	Pawelek clay loam	6.5	1.0	5.3	5.3	0.04	4.8
N-W-SW-NEB	Pawelek clay loam	7.8	1.1	5.7	5.2	0.07	1.9
N-W-SW-SWA	Pawelek clay loam	6.9	1.5	4.2	2.8	0.07	1.4
N-W-SW-SWB	Pawelek clay loam	7.6	1.0	8.4	8.4	0.20	0.2
N-W-NE-NWA	Pawelek clay loam	7.1	1.0	6.2	6.2	0.01	5.6
N-W-NE-NWB	Pawelek clay loam	8.0	1.1	7.0	6.4	0.02	1.6
N-W-NE-SEA	Pawelek clay loam	6.9	1.1	5.3	4.8	0.01	3.2
N-W-NE-SEB	Pawelek clay loam	7.7	1.1	6.7	6.1	0.01	4.1
N-E-S-NEA	Monteola clay	6.5	1.2	8.6	7.2	0.07	3.7
N-E-S-NEB	Monteola clay	7.0	1.1	7.8	7.1	0.05	1.4
N-E-S-SWA	Monteola clay	7.6	1.0	11	11	0.04	1.5
N-E-S-SWB	Monteola clay	7.8	0.7	9.2	13	0.03	1.9
N-E-N-NWA	Monteola clay	6.6	0.8	9.5	12	0.01	3.8
N-E-N-NWB	Monteola clay	7.2	0.9	10	11	0.01	1.2
N-E-N-SEA	Monteola clay	6.5	0.9	9.0	10	0.01	3.2
N-E-N-SEB	Monteola clay	6.9	1.0	10	10	0.01	4.6

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

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TABLE A-1. (continued)

Catahoula Formation
Coy City Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
S-NW-N-NA	Monteola clay	7.5	0.9	10	11	0.12	2.0
S-NW-N-NB	Monteola clay	7.8	1.1	12	11	0.07	4.4
S-NW-N-SA	Monteola clay	7.6	1.3	12	9.2	0.18	6.3
S-NW-N-SB	Monteola clay	7.7	1.6	11	6.9	0.06	6.3
S-NW-S-NWA	Monteola clay	7.8	0.8	9.7	12	0.31	3.3
S-NW-S-NWB	Monteola clay	7.9	0.7	6.4	9	0.12	3.9
S-NW-S-SEA	Monteola clay	8.0	0.9	9.1	10	0.11	5.2
S-NW-S-SEB	Monteola clay	7.9	0.5	6.4	13	0.03	2.4
S-SE-N-WA	Monteola clay	7.0	1.0	9.4	9.4	0.05	3.9
S-SE-N-WB	Monteola clay	7.8	0.9	9.9	11	0.01	6.9
S-SE-N-EA	Monteola clay	7.0	1.0	8.6	8.6	0.08	3.8
S-SE-N-EB	Monteola clay	7.7	1.0	11	11	0.10	0.3
S-SE-S-SWA	Monteola clay	7.0	1.0	8.6	8.6	0.10	2.3
S-SE-S-SWB	Monteola clay	7.2	0.8	9.2	12	0.05	2.5
S-SE-S-NEA	Monteola clay	7.3	0.8	9.1	11	0.09	5.8
S-SE-S-NEB	Monteola clay	7.9	0.9	9.7	11	0.05	4.0

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

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TABLE A-1. (continued)

Catahoula Formation
Comanche Hills Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
NE-E-NE-NEA	Monteola clay	7.8	0.8	11	14	0.16	-
NE-E-NE-NEB	Monteola clay	7.8	0.7	11	16	0.02	-
NE-E-NE-SWA	Monteola clay	7.9	1.2	10	8.5	0.09	-
NE-E-NE-SWB	Monteola clay	7.8	0.6	11	19	0.11	-
NE-E-SW-NWA	Monteola clay	7.2	0.8	7.2	9.0	0.16	-
NE-E-SW-NWB	Monteola clay	7.8	0.6	12	20	0.14	-
NE-E-SW-NW	(Bermudagrass)	-	1.4	6.1	4.4	-	-
NE-E-SW-SEA	Monteola clay	7.2	0.9	13	14	0.22	-
NE-E-SW-SEB	Monteola clay	7.9	0.5	13	26	0.15	-
NE-W-W-NEA	Monteola clay	7.8	0.6	11	19	0.12	-
NE-W-W-NEB	Monteola clay	7.7	0.6	11	19	0.03	-
NE-W-W-SWA	Monteola clay	7.7	0.7	11	16	0.13	-
NE-W-W-SWB	Monteola clay	7.8	0.8	12	15	0.07	-
NE-W-E-NEA	Monteola clay	7.8	0.8	11	14	0.11	-
NE-W-E-NEB	Monteola clay	7.8	0.8	9.9	12	0.07	-
NE-W-E-SWA	Monteola clay	7.8	0.8	10	13	0.17	-
NE-W-E-SWB	Monteola clay	7.8	0.8	10	13	0.13	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Catahoula Formation
Comanche Hills Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
SW-S-SW-NA	Clairville clay loam	7.9	0.6	9.8	16	0.11	-
SW-S-SW-NB	Clairville clay loam	7.9	0.6	8.3	14	0.15	-
SW-S-SW-SA	Clairville clay loam	7.8	0.6	9.5	16	0.17	-
SW-S-SW-SB	Clairville clay loam	8.0	0.6	9.4	16	0.09	-
SW-S-NE-NEA	Clairville clay loam	7.5	0.8	13	16	0.15	-
SW-S-NE-NEB	Clairville clay loam	7.8	0.7	13	18	0.09	-
SW-S-NE-SWA	Clairville clay loam	7.4	0.8	13	16	0.16	-
SW-S-NE-SWB	Clairville clay loam	7.8	0.7	12	17	0.09	-
SW-N-NE-NWA	Clairville clay loam	7.9	0.4	11	28	0.18	-
SW-N-NE-NWB	Clairville clay loam	7.8	0.6	11	18	0.11	-
SW-N-NE-SEA	Clairville clay loam	7.9	0.5	11	22	0.17	-
SW-N-NE-SEB	Clairville clay loam	7.8	1.0	12	12	0.11	-
SW-N-SW-NEA	Clairville clay loam	7.8	0.7	10	14	0.26	-
SW-N-SW-NEB	Clairville clay loam	7.7	0.8	10	13	0.12	-
SW-N-SW-SWA	Clairville clay loam	7.8	0.9	11	12	0.21	-
SW-N-SW-SWB	Clairville clay loam	7.8	0.9	8.5	9.4	0.11	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Oakville Formation
Garfield Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
NW-E-SE-NEA	Sarnosa fine sandy loam	7.9	1.1	-	-	0.28	-
NW-E-SE-NEB	Sarnosa fine sandy loam	8.0	0.9	-	-	0.27	-
NW-E-SE-SWA	Sarnosa fine sandy loam	8.1	1.1	-	-	0.15	-
NW-E-SE-SWB	Sarnosa fine sandy loam	7.9	1.1	-	-	0.23	-
NW-E-NW-NWA	Sarnosa fine sandy loam	8.1	1.1	-	-	0.25	-
NW-E-NW-NWB	Sarnosa fine sandy loam	8.1	1.1	-	-	0.20	-
NW-E-NW-SEA	Sarnosa fine sandy loam	8.2	1.2	-	-	0.21	-
NW-E-NW-SWB	Sarnosa fine sandy loam	8.2	1.1	-	-	0.25	-
NW-W-NE-SWA	Degola clay loam	7.9	0.7	-	-	0.17	-
NW-W-NE-SWB	Degola clay loam	8.2	0.7	-	-	0.18	-
NW-W-NE-NEA	Degola clay loam	7.9	0.8	-	-	0.17	-
NW-W-NE-NEB	Degola clay loam	8.4	0.8	-	-	0.11	-
NW-W-SW-NA	Degola clay loam	8.0	0.6	-	-	0.16	-
NW-W-SW-NB	Degola clay loam	8.2	0.8	-	-	0.15	-
NW-W-SW-SA	Degola clay loam	7.9	0.4	-	-	0.19	-
NW-W-SW-SB	Degola clay loam	8.1	0.6	-	-	0.17	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Oakville Formation

Garfield Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
SE-NE-SE-SEA	Sarnosa fine sandy loam	8.1	0.5	-	-	0.16	-
SE-NE-SE-SEB	Sarnosa fine sandy loam	8.1	1.0	-	-	0.11	-
SE-NE-SE-NWA	Sarnosa fine sandy loam	8.2	0.9	-	-	0.19	-
SE-NE-SE-NWB	Sarnosa fine sandy loam	8.1	0.9	-	-	0.23	-
SE-NE-NW-NWA	Sarnosa fine sandy loam	8.4	1.1	-	-	0.10	-
SE-NE-NW-NWB	Sarnosa fine sandy loam	8.4	0.9	-	-	0.26	-
SE-NE-NW-SEA	Sarnosa fine sandy loam	8.6	1.2	-	-	0.30	-
SE-NE-NW-SEB	Sarnosa fine sandy loam	8.4	0.9	-	-	0.16	-
SE-SW-E-SEA	Sarnosa fine sandy loam	8.0	1.3	-	-	0.27	-
SE-SW-E-SEB	Sarnosa fine sandy loam	7.9	0.7	-	-	0.13	-
SE-SW-E-NWA	Sarnosa fine sandy loam	8.0	0.5	-	-	0.16	-
SE-SW-E-NWB	Sarnosa fine sandy loam	8.0	0.6	-	-	0.25	-
SE-SW-W-NWA	Sarnosa fine sandy loam	8.2	0.6	-	-	0.18	-
SE-SW-W-NWB	Sarnosa fine sandy loam	8.4	0.5	-	-	0.16	-
SE-SW-W-SEA	Sarnosa fine sandy loam	8.0	0.7	-	-	0.22	-
SE-SW-W-SEB	Sarnosa fine sandy loam	8.3	0.4	-	-	0.11	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Oakville Formation

Kenedy Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
NW-SW-SW-EA	Runge fine sandy loam	8.4	0.5	-	-	0.12	-
NW-SW-SW-EB	Runge fine sandy loam	8.4	0.6	-	-	0.12	-
NW-SW-SW-WA	Runge fine sandy loam	8.2	0.5	-	-	0.11	-
NW-SW-SW-WB	Runge fine sandy loam	8.0	0.7	-	-	0.30	-
NW-SW-NE-EA	Runge fine sandy loam	8.1	0.8	-	-	0.16	-
NW-SW-NE-EB	Runge fine sandy loam	8.0	0.6	-	-	0.38	-
NW-SW-NE-WA	Runge fine sandy loam	8.1	0.7	-	-	0.05	-
NW-SW-NE-WB	Runge fine sandy loam	8.0	1.0	-	-	0.17	-
NW-NE-SE-EA	Wilco loamy fine sand	7.0	0.9	-	-	0.01	-
NW-NE-SE-EB	Wilco loamy fine sand	7.0	1.2	-	-	0.01	-
NW-NE-SE-WA	Wilco loamy fine sand	6.8	0.9	-	-	0.04	-
NW-NE-SE-WB	Wilco loamy fine sand	7.2	1.0	-	-	0.01	-
NW-NE-NW-EA	Wilco loamy fine sand	6.6	0.8	-	-	0.01	-
NW-NE-NW-EB	Wilco loamy fine sand	7.0	0.8	-	-	0.01	-
NW-NE-NW-WA	Wilco loamy fine sand	6.6	1.2	-	-	0.02	-
NW-NE-NW-WB	Wilco loamy fine sand	6.9	0.8	-	-	0.07	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Oakville Formation
Kenedy Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
SE-SE-SE-SWA	Danjer clay loam	8.4	0.9	-	-	0.16	-
SE-SE-SE-SWB	Danjer clay loam	8.4	0.9	-	-	0.15	-
SE-SE-SE-NEA	Danjer clay loam	8.2	0.7	-	-	0.12	-
SE-SE-SE-NEB	Danjer clay loam	8.2	0.6	-	-	0.08	-
SE-SE-NW-SWA	Pharr fine sandy loam	8.2	1.0	-	-	0.20	-
SE-SE-NW-SWB	Pharr fine sandy loam	7.9	1.1	-	-	0.21	-
SE-SE-NW-NEA	Pharr fine sandy loam	8.2	1.1	-	-	0.15	-
SE-SE-NW-NEB	Pharr fine sandy loam	8.3	0.9	-	-	0.13	-
SE-NW-E-NEA	Monteola clay	8.1	0.6	-	-	0.25	-
SE-NW-E-NEB	Monteola clay	8.1	0.6	-	-	0.26	-
SE-NW-E-SWA	Monteola clay	8.0	0.7	-	-	0.20	-
SE-NW-E-SWB	Monteola clay	8.1	0.6	-	-	0.31	-
SE-NW-W-NA	Monteola clay	7.9	0.8	-	-	0.23	-
SE-NW-W-NB	Monteola clay	7.9	1.1	-	-	0.19	-
SE-NW-W-SA	Monteola clay	8.0	1.1	-	-	0.24	-
SE-NW-W-SB	Monteola clay	8.3	0.6	-	-	0.12	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

Table A-1. (continued)

Oakville Formation
Ray Point Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
NE-SW-SW-SA	Sarnosa sandy clay loam	8.1	0.7	12	17	0.14	-
NE-SW-SW-SB	Sarnosa sandy clay loam	8.1	0.6	11	18	0.13	-
NE-SW-SW-NA	Sarnosa sandy clay loam	8.2	0.6	11	18	0.16	-
NE-SW-SW-NB	Sarnosa sandy clay loam	8.1	0.6	11	18	0.16	-
NE-SW-NE-SA	Sarnosa sandy clay loam	8.2	0.3	11	37	0.21	-
NE-SW-NE-SB	Sarnosa sandy clay loam	8.3	0.6	11	17	0.16	-
NE-SW-NE-NA	Sarnosa sandy clay loam	8.2	0.5	10	20	0.24	-
NE-SW-NE-NB	Sarnosa sandy clay loam	8.2	0.9	11	12	0.22	-
NE-NE-SE-SA	Monteola clay	8.3	0.5	8.5	17	0.21	-
NE-NE-SE-SB	Monteola clay	8.3	0.6	9.7	16	0.25	-
NE-NE-SE-NA	Monteola clay	8.2	0.8	8.6	11	0.13	-
NE-NE-SE-NB	Monteola clay	8.2	0.7	9.4	13	0.09	-
NE-NE-NW-SA	Monteola clay	8.1	0.6	11	18	0.20	-
NE-NE-NW-SB	Monteola clay	8.1	0.9	12	13	0.10	-
NE-NE-NW-NA	Monteola clay	8.0	0.9	11	12	0.20	-
NE-NE-NW-NB	Monteola clay	8.1	2.0	12	6.0	0.11	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

(continued)

TABLE A-1. (continued)

Oakville Formation

Ray Point Quadrangle

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
SW-SW-S-EA	Runge sandy clay loam	8.1	1.5	12	8.0	0.23	-
SW-SW-S-EB	Runge sandy clay loam	8.2	1.2	7.9	6.6	0.23	-
SW-SW-S-WA	Runge sandy clay loam	8.2	0.9	8.7	9.7	0.20	-
SW-SW-S-WB	Runge sandy clay loam	8.3	0.9	9.4	10	0.17	-
SW-SW-N-NEA	Runge sandy clay loam	8.1	0.8	13	16	0.24	-
SW-SW-N-NEB	Runge sandy clay loam	8.1	0.6	12	20	0.19	-
SW-SW-N-SWA	Runge sandy clay loam	8.2	1.2	10	8.0	0.20	-
SW-SW-N-SWB	Runge sandy clay loam	8.2	1.3	8.8	6.8	0.22	-
SW-NE-E-NA	Runge sandy clay loam	8.2	0.9	8.2	9.1	0.17	-
SW-NE-E-NB	Runge sandy clay loam	8.3	1.0	9.1	9.1	0.16	-
SW-NE-E-SA	Runge sandy clay loam	8.1	0.8	8.4	11	0.18	-
SW-NE-E-SB	Runge sandy clay loam	8.2	1.1	10	9.0	0.18	-
SW-NE-W-NEA	Runge sandy clay loam	8.1	1.0	8.9	8.9	0.20	-
SW-NE-W-NEB	Runge sandy clay loam	8.3	0.9	9.6	11	0.18	-
SW-NE-W-SWA	Runge sandy clay loam	8.3	1.7	9.0	5.3	0.37	-
SW-NE-W-SWB	Runge sandy clay loam	8.4	1.6	8.3	5.2	0.27	-

*All values are in ppm except pH and Cu/Mo; pH is in standard units.

TABLE A-2. MINING AND MINERALIZED AREA SAMPLES

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Stoeltje Area							
Stoeltje 1A	Monteola clay	8.1	0.7	-	-	-	-
Stoeltje 1B	Monteola clay	8.3	0.6	-	-	-	-
Stoeltje 2A	Pawelek clay loam	7.9	0.8	-	-	-	-
Stoeltje 2B	Pawelek clay loam	8.3	0.5	-	-	-	-
Stoeltje 3A	Monteola clay	6.4	0.9	-	-	-	-
Stoeltje 3B	Monteola clay	7.7	1.0	-	-	-	-
Stoeltje 4A	Pawelek clay loam	7.9	0.8	-	-	-	-
Stoeltje 4B	Pawelek clay loam	8.2	0.5	-	-	-	-
Stoeltje 5A	Monteola clay	8.1	0.8	-	-	-	-
Stoeltje 5B	Monteola clay	8.1	2.6	-	-	-	-
Stoeltje 6	Eroded spoil	8.2	0.8	-	-	-	-
Stoeltje 7	Eroded spoil	8.6	1.2	-	-	-	-
Stoeltje 8A	Reclaimed soil	8.1	2.4	-	-	-	-
Stoeltje 8B	Overburden	4.4	15	-	-	-	-
Stoeltje 9A	Reclaimed soil	7.6	0.8	-	-	-	-
Stoeltje 9B	Overburden	8.4	1.7	-	-	-	-
Stoeltje 10A	Danjer clay loam	8.1	1.3	-	-	-	-
Stoeltje 10B	Danjer clay loam	8.2	1.7	-	-	-	-
Stoeltje 11A	Danjer clay loam	7.0	1.1	-	-	-	-
Stoeltje 11B	Danjer clay loam	7.3	0.8	-	-	-	-
Stoeltje 12A	Danjer clay loam	6.0	1.3	-	-	-	-
Stoeltje 12B	Danjer clay loam	7.3	1.0	-	-	-	-
Stoeltje 13A	Monteola clay	6.7	1.0	-	-	-	-
Stoeltje 13B	Monteola clay	7.4	0.8	-	-	-	-
Stoeltje 14A	Monteola clay	7.9	0.9	-	-	-	-
Stoeltje 14B	Monteola clay	8.2	1.1	-	-	-	-

(continued)

TABLE A-2. (continued)

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Felder Area							
Felder 1A	Pharr fine sandy loam	8.2	0.6	8.5	14	-	-
Felder 1B	Pharr fine sandy loam	8.2	1.0	5.8	5.8	-	-
Felder 2A	Pharr fine sandy loam	8.4	1.2	6.3	5.3	-	-
Felder 2B	Pharr fine sandy loam	8.0	1.2	7.9	6.6	-	-
Felder 3A	Sandstone outcrop	9.2	7.6	3.6	0.47	-	-
Felder 4A	Sandstone outcrop	8.7	2.7	5.3	2.0	-	-
Felder 5A	Pharr fine sandy loam	8.5	2.3	4.6	2.0	-	-
Felder 5B	Pharr fine sandy loam	8.5	0.4	4.3	11	-	-
Felder 6A	Runge fine sandy loam	8.5	1.2	5.8	4.8	-	-
Felder 6B	Runge fine sandy loam	8.5	0.6	4.0	6.7	-	-
Felder 7A	Pharr fine sandy loam	8.8	1.2	3.4	2.8	-	-
Felder 7B	Pharr fine sandy loam	8.5	1.8	5.0	2.8	-	-
Felder 8A	Pharr fine sandy loam	8.4	1.5	4.5	3.0	-	-
Felder 8B	Pharr fine sandy loam	8.4	0.1	5.1	51	-	-
Felder 9A	Monteola clay	7.8	0.8	5.4	6.8	-	-
Felder 9B	Monteola clay	8.2	1.4	5.9	4.2	-	-
Felder 10	Ore	8.0	26	7.6	0.29	-	-
Felder 11A	Runge fine sandy loam	8.2	1.9	7.2	3.8	-	-
Felder 11B	Runge fine sandy loam	8.2	1.4	9.5	6.8	-	-

(continued)

TABLE A-2. (continued)

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Weddington Area							
Weddington 1A	Sinton-Zavala	8.5	8.8	14	1.6	0.87	-
Weddington 1B	Sinton-Zavala	8.4	5.5	12	2.1	0.39	-
Weddington 2A	Monteola clay	8.6	0.8	7.2	9.0	0.22	-
Weddington 2B	Monteola clay	9.3	1.0	8.9	8.9	0.14	-
Weddington 3A	Monteola clay	8.4	1.4	-	-	0.14	-
Weddington 3B	Monteola clay	9.0	1.3	-	-	0.14	-
Weddington 4A	Monteola clay	8.5	0.6	-	-	0.17	-
Weddington 4B	Monteola clay	9.0	0.7	-	-	0.08	-
Weddington 5A	Monteola clay	8.8	0.7	-	-	0.10	-
Weddington 5B	Monteola clay	8.8	2.2	-	-	0.21	-
Weddington 6A	Monteola clay	8.7	0.6	8.0	13	0.14	-
Weddington 6B	Monteola clay	9.3	0.7	7.5	11	0.12	-
Weddington 7A	Sinton-Zavala	8.1	50	11	0.22	6.6	-
Weddington 7B	Sinton-Zavala	8.1	35	10	0.29	0.28	-
Weddington 8A	Monteola clay	8.4	0.7	7.6	11	0.18	-
Weddington 8B	Monteola clay	9.1	0.6	9.8	16	0.10	-
Weddington 9A	Monteola clay	8.2	0.9	11	12	0.15	-
Weddington 9B	Monteola clay	8.9	0.7	7.9	11	0.12	-
Weddington 10A	Sinton-Zavala	8.3	1.6	11	6.9	0.16	-
Weddington 10B	Sinton-Zavala	8.4	21	10	0.48	0.79	-
Weddington 11A	Pawelek clay loam	8.6	1.0	-	-	0.20	-
Weddington 11B	Pawelek clay loam	8.9	0.9	-	-	0.14	-
Weddington 12A	Monteola clay	8.3	0.9	-	-	0.14	-
Weddington 12B	Monteola clay	8.8	1.0	-	-	0.13	-
Weddington 13A	Sinton-Zavala	8.7	8.4	11	1.3	1.5	-
Weddington 13B	Sinton-Zavala	8.5	14	11	0.79	0.43	-

(continued)

TABLE A-2. (continued)

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Weddington 14A	Sinton-Zavala	8.4	0.8	-	-	0.18	-
Weddington 14B	Sinton-Zavala	8.5	0.8	-	-	0.19	-
Weddington 15A	Sinton-Zavala	8.2	4.6	-	-	0.45	-
Weddington 15B	Sinton-Zavala	8.3	2.2	-	-	0.33	-
Weddington 16A	Monteola clay	8.5	1.0	-	-	0.31	-
Weddington 16B	Monteola clay	8.8	1.0	-	-	0.42	-
Weddington 17A	Reclaimed soil	8.2	5.7	12	2.1	1.5	-
Weddington 17B	Overburden	6.7	6.8	9.7	1.4	1.0	-
Weddington 18A	Eroded spoil	7.8	3.6	7.5	2.1	0.27	-
Weddington 18B	Monteola clay	8.5	1.4	9.1	6.5	0.15	-
Weddington 19A	Monteola clay	8.5	1.4	13	9.3	0.25	-
Weddington 19B	Monteola clay	8.7	0.8	8.0	10	0.18	-
Weddington 20A	Monteola clay	7.5	1.9	4.0	2.1	0.17	-
Weddington 20B	Monteola clay	7.9	4.3	11	2.6	0.58	-
Weddington 21A	Eroded spoil	8.9	6.9	12	1.7	0.47	-
Weddington 21B	Monteola clay	8.2	4.2	12	2.9	0.28	-
Weddington 22A	Monteola clay	8.4	5.1	9.7	1.9	0.88	-
Weddington 22B	Monteola clay	9.0	2.1	13	6.2	0.36	-
Weddington 23A	Cestohowa fine sandy loam	7.1	1.8	2.0	1.1	0.36	-
Weddington 23B	Cestohowa fine sandy loam	7.0	1.6	2.5	1.6	0.12	-
Weddington 24A	Sinton-Zavala	8.3	7.4	11	1.5	1.2	-
Weddington 24B	Sinton-Zavala	8.6	5.7	9.5	1.7	0.17	-

(continued)

TABLE A-2. (continued)

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Weddington 25A	Clairville clay loam	8.1	0.8	7.3	9.1	0.11	-
Weddington 25B	Clairville clay loam	8.6	0.9	8.2	9.1	0.15	-
Weddington 26A	Sinton-Zavala	8.2	11	6.8	0.62	-	-
Weddington 26B	Sinton-Zavala	8.8	11	6.7	0.61	-	-
Weddington 26C	(Bermudagrass)	-	23	8.3	0.36	-	-
Weddington 27A	Monteola clay	8.6	1.0	6.1	6.1	-	-
Weddington 27B	Monteola clay	7.9	1.1	6.2	5.6	-	-
Weddington 27C	(Bermudagrass)	-	3.6	46	13	-	-
Weddington 28A	Monteola clay	8.3	1.1	7.0	6.4	-	-
Weddington 28B	Monteola clay	8.4	1.1	7.0	6.4	-	-
Weddington 28C	(Bermudagrass)	-	2.9	4.9	1.7	-	-
Weddington 29A	Sinton-Zavala	8.2	6.1	7.3	1.2	-	-
Weddington 29B	Sinton-Zavala	8.1	7.3	8.8	1.2	-	-
Weddington 29C	(Bermudagrass)	-	18	8.6	0.48	-	-
Weddington 30A	Monteola clay	8.1	0.4	5.4	1.4	-	-
Weddington 30B	Monteola clay	8.1	1.2	4.9	4.1	-	-
Weddington 30C	(Grass)	-	1.8	4.6	2.6	-	-
Weddington 31A	Sinton-Zavala	8.6	3.7	6.7	1.8	-	-
Weddington 31B	Sinton-Zavala	8.3	1.3	5.6	4.3	-	-
Weddington 31C	(Bermudagrass)	-	1.9	80	42	-	-
Weddington 31D	Clay outcrop	-	1.6	4.8	3.0	-	-

(continued)

TABLE A-2. (continued)

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Nieschwitz Area							
Nieschwitz 1A	Tordia clay	8.4	5.9	5.3	0.90	0.54	34
Nieschwitz 1B	Tordia clay	8.7	1.8	4.5	2.5	0.34	15
Nieschwitz 2A	Tordia clay	8.2	4.2	7.8	1.9	0.53	41
Nieschwitz 2B	Clay bedrock	8.9	8.1	8.5	1.1	0.16	11
Nieschwitz 3A	Tordia clay	7.2	16	5.4	0.34	0.42	7.4
Nieschwitz 4A	Sandstone outcrop	7.8	73	7.1	0.10	0.50	115
Nieschwitz 5A	Tordia clay	8.5	17	4.8	0.28	0.34	45
Nieschwitz 5B	Tordia clay		16	5.2	0.33	0.73	4.8
Nieschwitz 6A	Tordia clay	7.1	9.6	6.9	0.72	0.40	18
Nieschwitz 6B	Tordia clay	6.8	12	5.4	0.45	0.46	17
Nieschwitz 7A	Tordia clay	8.4	3.5	4.5	1.3	0.22	2.9
Nieschwitz 7B	Tordia clay	8.2	2.2	3.3	1.5	0.26	7.0
Nieschwitz 8A	Tordia clay	7.1	1.7	4.6	2.7	0.47	6.3
Nieschwitz 8B	Tordia clay	8.0	4.6	3.7	0.80	0.59	8.7
Culpepper Area							
Culpepper 1A	Pawelek clay loam	7.4	8.4	7.1	0.85	-	-
Culpepper 1B	Pawelek clay loam	8.1	2.2	5.8	2.6	-	-
Culpepper 2A	Pawelek clay loam	7.3	3.5	6.5	1.9	-	-
Culpepper 2B	Pawelek clay loam	7.8	4.0	6.3	1.6	-	-
Culpepper 3A	Pawelek clay loam	7.3	2.0	6.4	3.2	-	-
Culpepper 3B	Pawelek clay loam	8.8	2.2	7.7	3.5	-	-
Culpepper 4A	Pawelek clay loam	7.3	2.4	6.3	2.6	-	-
Culpepper 4B	Pawelek clay loam	7.9	3.4	7.6	2.2	-	-
Culpepper 5	Cestohowa fine sandy loam	6.1	1.4	2.6	1.9	-	-
Culpepper 6	Cestohowa fine sandy loam	6.1	1.2	3.1	2.6	-	-
Culpepper 7	Cestohowa fine sandy loam	6.3	1.3	3.9	3.0	-	-
Culpepper 8	Cestohowa fine sandy loam	6.3	3.2	5.9	1.8	-	-

(continued)

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TABLE A-2. (continued)

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Lyssy Area							
Lyssy 1	Monteola clay	7.9	4.0	9.9	2.5	-	-
Lyssy 2	Monteola clay	8.0	6.8	7.4	1.1	-	-
Lyssy 3	Monteola clay	7.4	2.5	8.0	3.2	-	-
Lyssy 4	Monteola clay	8.2	1.9	10	5.3	-	-
Lyssy 5	Monteola clay	7.9	2.4	9.6	4.0	-	-
Lyssy 6	Monteola clay	8.0	12	7.4	0.62	-	-
Boso Area							
Boso 1A	Picosa loam	7.6	53	8.0	0.15	1.2	42
Boso 1B	Picosa loam	6.9	98	6.8	0.07	1.1	95
Boso 2A	Picosa loam	6.2	23	11	0.48	9.1	51
Boso 2B	Picosa loam	6.8	22	11	0.50	14	48
Boso 3	Disturbed area	7.3	369	4.4	0.01	16	272
Boso 4A	Picosa loam	6.4	26	5.7	0.22	2.2	49
Boso 4B	Picosa loam	8.4	57	6.6	0.12	1.3	66
Boso 5A	Picosa loam	7.7	6.5	7.2	1.1	0.96	16
Boso 5B	Picosa loam	8.0	4.3	7.5	1.7	0.35	9.3
Boso 6A	Picosa loam	7.4	4.1	8.7	2.1	0.37	9.5
Boso 6B	Picosa loam	8.3	5.6	8.7	1.6	0.48	8.6
Boso 7A	Picosa loam	7.7	49	13	0.27	3.1	68
Boso 7B	Weathered bedrock	6.8	856	3.8	0.004	3.8	450
Boso 8	Spoil	5.7	11200	7.0	0.0006	15	482
Boso 9A	Picosa loam	8.1	6.2	7.6	1.2	0.66	41
Boso 9B	Picosa loam	8.4	5.3	8.5	1.6	0.58	17
Boso 10A	Picosa loam	6.4	3.9	9.8	2.5	0.72	9.0
Boso 10B	Picosa loam	6.8	3.3	8.4	2.6	0.99	8.7

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TABLE A-2. (continued)

LOCATION	SOIL	pH	Mo	Cu	Cu/Mo	Se	As
Boso 11	Spoil	7.3	548	4.9	0.009	4.6	417
Boso 12A	Picosa loam	7.1	26	8.4	0.32	2.1	18
Boso 12B	Picosa loam	8.2	18	7.6	0.42	1.9	93
Boso 13A	Picosa loam	6.6	14	6.1	0.44	0.89	49
Boso 13B	Picosa loam	7.5	23	8.5	-	1.1	40
Tordillo Area							
Tordillo 1A	Sinton-Zavala	6.8	3.2	3.7	1.2	-	-
Tordillo 1B	Sinton-Zavala	7.8	8.3	3.5	0.42	-	-
Tordillo 2A	Sinton-Zavala	7.2	0.9	2.7	3.0	-	-
Tordillo 2B	Sinton-Zavala	7.1	3.2	3.4	1.1	-	-
Tordillo 2C	(Bermudagrass)	-	9.8	10	1.0	-	-
Tordillo 3A	Sinton-Zavala	7.5	0.5	2.6	5.2	-	-
Tordillo 4A	Sinton-Zavala	7.3	1.0	4.2	4.2	-	-
Tordillo 4B	Sinton-Zavala	6.8	2.6	3.6	1.4	-	-
Tordillo 5	Sinton-Zavala	6.7	5.4	10	1.9	-	-
Tordillo 6A	Sinton-Zavala	7.6	2.5	4.0	1.6	-	-
Tordillo 6B	Sinton-Zavala	6.5	6.8	5.1	0.75	-	-
Tordillo 6C	(Bermudagrass)	-	2.5	8.8	3.5	-	-
S 1A	Tordia clay	8.5	1.5	-	-	0.33	-
S 1B	Tordia clay	8.9	0.8	-	-	0.35	-
S 2A	Tordia clay	8.3	1.1	-	-	0.43	-
S 2B	Tordia clay	8.5	1.1	-	-	0.31	-
S 3A	Sinton-Zavala	7.0	2.1	-	-	0.33	-
S 3B	Sinton-Zavala	7.1	1.4	-	-	0.25	-
S 4A	Sinton-Zavala	7.9	2.8	-	-	0.37	-
S 5	Tailings	7.0	40	-	-	1.0	-

TABLE A-3. ANALYSIS OF VARIANCE

MOLYBDENUM ANALYSIS:

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F-Ratio
Whitsett Fashing:				
4 km	1	1.128	1.128	0.45
500 m	2	5.015	2.51	31.14**
64 m	4	0.322	0.081	0.604
8 m	8	1.067	0.133	0.555
A-B	16	3.841	0.24	
TOTAL	31	11.373		
Catahoula Ecleto:				
4 km	1	.479	.479	.308
500 m	2	3.113	1.557	3.4
64 m	4	1.831	.458	.918
8 m	8	3.989	.499	6.11**
A-B	16	1.31	.082	
TOTAL	31	10.717		
Comanche Hills:				
4 km	1	.0434	.0434	15.761
500 m	2	.0055	.0028	.0256
64 m	4	.4301	.1075	3.671
8 m	8	.2344	.0293	.571
A-B	16	.8214	.0513	
TOTAL	31	1.5348		

* Significant at 95% confidence level.
** Significant at 99% confidence level.

(continued)

TABLE A-3. (continued)

MOLYBDENUM ANALYSIS:

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F-Ratio
Falls City:				
4 km	1	0.1581	0.158	0.307
500 m	2	1.031	0.516	5.98
64 m	4	0.345	0.086	3.70
8 m	8	0.186	0.023	0.191
A-B	16	1.948	0.122	
TOTAL	31	3.668		
Coy City:				
4 km	1	.079	0.079	1.491
500 m	2	0.106	0.053	0.35
64 m	4	0.598	0.150	4.06*
8 m	8	0.295	0.037	1.36
A-B	16	0.432	0.027	
TOTAL	31	1.509		
Oakville Garfield:				
4 km	1	.118	.118	.154
500 m	2	1.524	.762	7.14*
64 m	4	.427	.107	1.65
8 m	8	.519	.065	1.25
A-B	16	.831	.052	
TOTAL	31	3.419		
Kenedy:				
4 km	1	.006	.006	.019
500 m	2	.630	.315	2.13
64 m	4	.591	.148	5.18*
8 m	8	.228	.029	.77
A-B	16	.590	.037	
TOTAL	31	2.045		

* Significant at 95% confidence level.
** Significant at 99% confidence level.

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TABLE A-3. (continued)

MOLYBDENUM ANALYSIS:

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F-Ratio
Ray Point:				
4 km	1	1.516	1.516	0.89
500 m	2	0.44	0.22	1.36
64 m	4	0.649	0.162	.87
8 m	8	1.488	0.186	3.02*
A-B	16	0.985	0.062	
TOTAL	31	5.077		

Variance Components

Level	Difference	Sample Size	Variance Component	Percent Variance
Whitsett Fashing:				
4 km	-1.379	16	0	0
500 m	2.427	8	0.30	55.8
64 m	-0.053	4	0	0
8 m	-.107	2	0	0
A-B	0.24	1	0.24	44.2
Catahoula Ecleto:				
4 km	-1.08	16	0	0
500 m	1.099	8	0.137	32.1
64 m	-.041	4	0	0
8 m	.417	2	0.208	48.8
A-B	.0816	1	0.082	19.1
Comanche Hills:				
4 km	0.041	16	.0025	3.5
500 m	-.105	8	0	0
64 m	.078	4	.0196	26.6
8 m	-.022	2	0	0
A-B	.051	1	.051	69.9

* Significant at 95% confidence level.
** Significant at 99% confidence level.

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TABLE A-3. (continued)

MOLYBDENUM ANALYSIS:

Variance Components

Level	Difference	Sample Size	Variance Component	Percent Variance
Falls City:				
4 km	-.357	16	0	0
500 m	.429	8	0.0537	28.1
64 m	.063	4	.0157	8.2
8 m	-.098	2	0	0
A-B	.122	1	0.122	63.7
Coy City:				
4 km	.026	16	.0016	2.6
500 m	-.097	8	0	0
64 m	.113	4	0.0282	45.7
8 m	.0098	2	0.0049	7.0
A-B	.027	1	0.027	43.8
Oakville Garfield:				
4 km	-.645	16	0	0
500 m	.655	8	0.082	54.3
64 m	.042	4	0.010	6.9
8 m	.013	2	0.0065	4.3
A-B	.052	1	0.052	34.4
Kenedy:				
4 km	-.309	16	0	0
500 m	.167	8	0.021	23.8
64 m	.119	4	0.030	34.0
8 m	-.008	2	0	0
A-B	.037	1	0.037	42.1
Ray Point:				
4 km	1.296	16	.081	38.2
500 m	.058	8	.007	3.4
64 m	-.024	4	0	0
8 m	.125	2	.0623	29.4
A-B	.062	1	.0675	29.0

* Significant at 95% confidence level.
** Significant at 99% confidence level.

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TABLE A-3. (continued)

SELENIUM ANALYSIS:

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F-Ratio
Fashing:				
4 km	1	5.5178	5.5178	0.6491
500 m	2	17.0026	8.5013	2.4824
64 m	4	13.6986	3.4247	5.0665*
8 m	8	5.4076	0.6759	1.2357
A-B	16	8.7159	0.5470	
TOTAL	31	16.1634		
Ecleto:				
4 km	1	0.6406	0.6406	0.207
500 m	2	6.1977	3.099	6.753
64 m	4	1.836	0.459	3.019
8 m	8	1.216	0.152	0.388
A-B	16	6.273	0.392	
TOTAL	31			
Comanche Hills:				
4 km	1	0.6636	0.6636	4.31
500 m	2	0.308	0.1540	0.375
64 m	4	1.644	0.411	3.756
8 m	8	0.875	0.109	0.363
A-B	16	4.825	0.302	
TOTAL	31	8.3157		
Falls City:				
4 km	1	0.130	0.130	0.099
500 m	2	2.635	1.318	7.747*
64 m	4	0.680	0.17	0.523
8 m	8	2.599	0.325	0.831
A-B	16	6.254	0.391	
TOTAL	31	12.298		

* Significant at 95% confidence level.
** Significant at 99% confidence level.

(continued)

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TABLE A-3. (continued)

SELENIUM ANALYSIS:

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F-Ratio
Coy City:				
4 km	1	9.28	9.28	9.34
500 m	2	1.99	0.99	0.33
64 m	4	12.13	3.03	5.44*
8 m	8	4.46	0.56	1.851
A-B	16	4.82	0.30	
TOTAL	31	32.85		
Garfield:				
4 km	1	0.0155	0.0155	0.064
500 m	2	0.481	0.240	5.15
64 m	4	0.187	0.047	0.81
8 m	8	0.461	0.058	0.735
A-B	16	1.255	0.078	
TOTAL	31	2.3995		
Kenedy:				
4 km	1	12.96	12.96	1.29
500 m	2	20.03	10.01	70.6**
64 m	4	0.567	0.142	0.3
8 m	8	3.76	0.47	1.97
A-B	16	3.82	0.239	
TOTAL	31	41.137		
Ray Point:				
4 km	1	0.484	0.484	12.23
500 m	2	0.079	0.0396	0.33
64 m	4	0.486	0.1215	1.0
8 m	8	0.963	0.1204	2.98*
A-B	16	0.647	0.04	
TOTAL	31	2.659		

* Significant at 95% confidence level.
** Significant at 99% confidence level.

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TABLE A-3. (continued)

SELENIUM ANALYSIS:

Variance Components

Level	Difference	Sample Size	Variance Component	Percent Variance
Fashing:				
4 km	-2.984	16	0	0
500 m	5.077	8	0.635	32.8
64 m	2.749	4	0.687	35.5
8 m	0.129	2	0.065	3.3
A-B	0.547	1	0.547	28.3
Ecleto:				
4 km	-2.46	16	0.0	0
500 m	2.64	8	0.33	41.3
64 m	0.31	4	0.077	9.6
8 m	-0.24	2	0.0	0
A-B	0.39	1	0.39	49.1
Comanche Hills:				
4 km	0.51	16	0.0319	7.8
500 m	-0.257	8	0.0	0
64 m	0.301	4	0.0754	18.4
8 m	-0.192	2	0.0	0
A-B	0.302	1	0.3016	73.8
Falls City:				
4 km	-1.187	16	0	0
500 m	1.147	8	0.143	26.8
64 m	-0.155	4	0	0
8 m	-0.066	2	0	0
A-B	0.391	1	0.391	73.2
Coy City:				
4 km	8.285	16	0.518	33.1
500 m	02.039	8	0	0
64 m	2.474	4	0.019	39.5
8 m	0.256	2	0.128	8.2
A-B	0.301	1	0.30	19.2

* Significant at 95% confidence level.
** Significant at 99% confidence level.

(continued)

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TABLE A-3. (continued)

SELENIUM ANALYSIS:

Variance Components

Level	Difference	Sample Size	Variance Component	Percent Variance
Garfield:				
4 km	-0.225	16	0	0
500 m	0.194	8	0.024	23.6
64 m	-0.011	4	0	0
8 m	-0.021	2	0	0
A-B	0.078	1	0.078	70.4
Kenedy:				
4 km	2.94	16	0.184	10.0
500 m	9.87	8	1.234	69.6
64 m	-0.328	4	0	0
8 m	0.23	2	0.116	6.5
A-B	0.239	1	0.239	13.5
Ray Point:				
4 km	0.44	16	0.028	25.6
500 m	-0.082	8	0	0
64 m	0.001	4	0.00028	.03
8 m	0.08	2	0.040	36.8
A-B	0.04	1	0.04	37.3

* Significant at 95% confidence level.
** Significant at 99% confidence level.

(continued)

TABLE A-3. (continued)

COPPER ANALYSIS:

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F-Ratio
Fashing:				
4 km	1	0.5478	0.5478	4.9625
500 m	2	0.2208	0.1104	1.0902
64 m	4	0.4050	0.1013	2.9548
8 m	8	0.2742	0.0343	2.5045
A-B	16	0.2189	0.0137	
Coy City:				
4 km	1	0.409	0.409	1.029
500 m	2	0.795	0.398	4.99
64 m	4	0.318	0.0796	10.577**
8 m	8	0.060	0.0075	0.24
A-B	16	0.498	0.0311	
Comanche Hills:				
4 km	1	.0011	.0011	.4373
500 m	2	.0049	.0025	.0374
64 m	4	.2626	.0656	4.2172*
8 m	8	.1245	.0156	1.2434
A-B	16	.2003	.0125	
Ray Point:				
4 km	1	.097	.097	2.34
500 m	2	.083	.041	1.03
64 m	4	.160	.040	3.22
8 m	8	.100	.013	1.27
A-B	16	.157	.010	

* Significant at 95% confidence level.
** Significant at 99% confidence level.

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TABLE A-3. (continued)

COPPER ANALYSIS:

Variance Components

Level	Difference	Sample Size	Variance Component	Percent Variance
Fashing:				
4 km	.4374	16	.0273	39.5
500 m	.009	8	.001	1.7
64 m	.0669	4	.016	24.2
8 m	.0206	2	.0103	14.9
A-B	.0137	1	.0137	19.8
Coy City:				
4 km	.01165	16	0.00073	0.8
500 m	0.318	8	0.03974	44.4
64 m	0.0721	4	0.01802	20.0
8 m	-0.024	2	0	0
A-B	0.031	1	0.03112	34.7
Comanche Hills:				
4 km	-.001	16	0	0
500 m	-.06	8	0	0
64 m	.05	4	.013	47.1
8 m	.003	2	.002	5.4
A-B	.013	1	.013	47.1
Ray Point:				
4 km	.0552	16	.0035	15.9
500 m	.001	8	.0002	0.7
64 m	.028	4	.0069	31.9
8 m	.0026	2	.0013	6.1
A-B	.0098	1	.0098	45.3

* Significant at 95% confidence level.
** Significant at 99% confidence level.

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TABLE A-3. (continued)

ARSENIC ANALYSIS:

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F-Ratio
Fashing:				
4 km	1	0.1894	0.1894	2.9043
500 m	2	0.1304	0.0652	5.2197
64 m	4	0.05	0.0125	0.1576
8 m	8	0.6342	0.0793	1.3719
A-B	16	0.9245	0.0578	
TOTAL	31	1.9284		
Coy City:				
4 km	1	.2605	.261	5.3387
500 m	2	.0976	.0488	.42
64 m	4	.465	.1162	.699
8 m	8	1.331	.1663	1.6697
A-B	16	1.594	.0996	

Variance Components

Level	Difference	Sample Size	Variance Component	Percent Variance
Fashing:				
4 km	.1242	16	.0078	9.4
500 m	.0527	8	.0066	8.0
64 m	-.067	4	0	0
8 m	.02	2	.011	13.0
A-B	.058	1	.058	69.7
Coy City:				
4 km	.2118	16	.01323	9.1
500 m	-.0674	8	0	0
64 m	-.05	4	0	0
8 m	.0667	2	.0334	22.8
A-B	.0996	1	.0996	68.1

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TABLE A-4. CORRELATION COEFFICIENTS

Formation or Area	Quadrangle	Correlation Coefficients		
		Cu - Mo	Mo - As	Mo - Se
Whitsett	Fashing	-0.14	0.14	0.61
Catahoula	Ecleto	0.33	-	-0.03
	Falls City	-	-	0.33
	Coy City	-0.02	0.13	0.0
	Comanche Hills	0.04	-	-0.04
Oakville	Garfield	-	-	0.45
	Kenedy	-	-	-0.26
	Ray Point	0.50	-	0.30
Nieschwitz	-	0.34	0.87	0.20
Felder	-	-0.34	-	-
Boso	-	0.06	0.65	0.04

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APPENDIX B: ANALYTICAL METHODS*

1. Total Molybdenum in Soils

The procedure of Quin and Brooks (1975) modified by our laboratory was used. Weigh 0.5 g (less than 100 mesh) sample and 2.5 g $KHSO_4$ into a test tube and fuse the content over a Fisher burner. After cooling, the content is dissolved in 4N re-distilled HCl in a boiling water bath. Clear solution is separated by filtration. Mo in filtrate is complexed by dithiol in presence of KI, ascorbic acid, and thioglycolic acid. The green-colored Mo-dithiol is extracted with amyl acetate and measured at 682 mμ using a Pye-Unicam SP8-100 spectrophotometer. Standards and blank are run exactly the same way as samples.

Total Molybdenum in Grass Samples

One gram of finely ground grass (less than 100 mesh) is ashed at 550°C. The ash is then fused with $KHSO_4$. The analytical procedure for Mo is identical with that for soils as described above.

2. Total Selenium by Fluorometry

Weigh 0.5 g soil sample (less than 100 mesh) (one gram should be used for plant sample) into a test tube and digested with re-distilled HNO_3 and concentrated H_2SO_4 (free of Se) until complete removal of HNO_3 (Fine, 1965). The content is made to a final volume of 50 ml with de-ionized water. An aliquot of the clear solution is acidified with 6N distilled HCl followed by adjusting the solution to a constant pH of 2.0 with H_3PO_4 and NH_4OH. The test tubes are then wrapped tightly with aluminum foil to prevent light penetration before addition of diaminonaphthalene (DAN). Se is quantitatively complexed by DAN at 50°-60°C in a 15-minute water bath. After cooling, the Se-DAN complex is extracted into cyclohexane and measured on a fluorometer. Standards and blank are run the same way as the samples (Michael and White, 1976).

3. Total Arsenic in Soils and Plant Material

Weigh 0.5 g of sample (less than 100 mesh) into a graphite crucible followed by addition of 2.5 g of flux ($MgO+K_2CO_3$ at a ratio of 1 to 3 by weight). Mix the sample and the flux thoroughly before fusing at 900°C for 20 min. (Jeffery, 1970). The flux is dissolved in re-distilled HCl. An aliquot of the solution is distilled in presence of hydrazine sulfate and HBr using a distillation apparatus described elsewhere (Bremner, 1965). The distillate is trapped in re-distilled HNO_3. Complete distillation requires only a few minutes. Arsenic in distillate is analyzed by IL650 flameless atomic absorption using a graphite furnace (Ho and others, 1978).

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*Prepared by Clara Ho, Mineral Studies Laboratory, Bureau of Economic Geology, The University of Texas at Austin.

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4. Copper in Soils and Plant Materials

Weigh one gram of soil (less than 100 mesh) into a test tube. The sample is digested with re-distilled HNO_3 followed by further digestion with re-distilled HCl until near complete removal of excess acids. The content is dissolved in de-ionized water and filtered to obtain clear extract. Copper in filtrate is analyzed by IL650 atomic absorption spectrophotometer using acetylene-air flame.

Plant material (less than 100 mesh) is analyzed for Copper in exactly the same fashion as the soils with exception that dry-ashing at 550°C prior to acid digestion is carried out (Ho and DuPont, 1978).

5. Soil pH

Five grams of undisturbed natural soil is added to 10 ml de-ionized water. Stir the slurry with glass rod for complete dispersion. Measure pH of the slurry after 15 min. equilibration using a glass electrode and calomel electrode as reference.

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TABLE B-1. ANALYSES OF REFERENCE SAMPLES

ENVIRONMENTAL PROTECTION AGENCY QUALITY CONTROL SAMPLES FOR TRACE METAL ANALYSIS

	Arsenic (mg/l)		Selenium (mg/l)		Copper (mg/l)	
Sample	Reported	Found	Reported	Found	Reported	Found
1	26	26.3	5.2	5.0	16	17
2	109	100	26	29.2	72	76
3	154	159	44	47.8	102	105

UNITED STATES GEOLOGICAL SURVEY GEOCHEMICAL EXPLORATION REFERENCE SAMPLES

	Molybdenum (ppm)[A]		Selenium (ppm)[B]	
Sample	Reported	Found	Reported	Found[C]
GXR-1	14	19	-	-
GXR-2	1.3	1.0	-	0.39±0.04(8)
GXR-3	6.0	2.1	-	-
GXR-4	258	250	-	-
GXR-5	30	27	-	0.78±0.08(21)
GXR-6	2.0	2.3	-	-

A. Reported concentrations are median values from Allcott and Lakin (1974).

B. Various concentrations, but no accepted values, are reported by Crenshaw and Lakin (1974).

C. Mean ± standard deviation (number of analyses).

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